



DIELECTRIC RELAXATION OF ACETONE IN BENZENE SOLUTION USING MICROWAVE ABSORPTION DATA

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ABSTRACT

The dielectric permittivity (ϵ') and dielectric loss (ϵ'') for dilute solutions of acetone (CH_3COCH_3) in benzene solution have been measured at 9.88 GHz for different temperatures (25, 30, 35 and 40°C) by using standard microwave techniques. Using the single frequency concentration variational method; the dielectric relaxation time (τ) and dipole moment (μ) at various temperatures have been calculated. It is observed that dielectric relaxation process can be treated as the rate process, just like the viscous flow. Based on above microwave absorption data, monomer structure of acetone in benzene solution has been inferred. The presence of solute-solvent molecular associations in benzene solution has not been proposed. Energy parameters (ΔH_e , ΔF_e , ΔS_e) for dielectric relaxation process of acetone in benzene at different temperatures (25, 30, 35 and 40°C) have been calculated and compared with the corresponding energy parameters (ΔH_η , ΔF_η , ΔS_η) of viscous flow process.

Key words: Dielectric relaxation, Microwave absorption, Acetone, Benzene

INTRODUCTION

Acetone (CH_3COCH_3) is recognized as the polar non-aqueous aprotic solvent having dielectric permittivity of $\epsilon' = 20.7$ at 25°C and dipole moment of $\mu = 2.80$ D. Its boiling point is 57°C. Acetone is slightly acidic and it has the physical properties such as high evaporation rate, low viscosity and high miscibility with water and several organic solvents. Because of its ability to undergo addition, oxidation/reduction and condensation reactions, acetone is used as the raw material in chemical synthesis of many commercial products like plastic, paints, rubber etc. Acetone is also used as drying agent, due to the readiness with which it mixes with water and its volatility. This molecular aspect of

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acetone (CH_3COCH_3) motivated the authors to study the molecular behavior of acetone in benzene solution. The study of dielectric relaxation of polar molecules from microwave absorption data has raised the interest to understand the solute-solute and solute-solvent type of molecular associations in the non-polar medium¹⁻⁵. Dielectric data obtained from microwave absorption studies is expected to throw light on solute-solvent type of molecular associations present in the solution. Microwaves are sensitive to weaker molecular interactions. The present paper is related with the dielectric relaxation studies of acetone in benzene at different temperatures (25, 30, 35 and 40°C) from microwave absorption studies at 9.88 GHz. It is found that, acetone occurs in the monomer form in the benzene solution. The presence of solute-solvent molecular associations in benzene solution has not been proposed in the entire concentration range. It is found that dielectric relaxation process of acetone in benzene solution can be treated as the activated process. Energy parameters (ΔH_ε , ΔF_ε , ΔS_ε) for dielectric relaxation process and for viscous flow process (ΔH_η , ΔF_η , ΔS_η) have been calculated at different temperatures (25, 30, 35 and 40°C). The energy parameters of dielectric relaxation process and viscous flow process have been compared with each other.

EXPERIMENTAL

Acetone (CH_3COCH_3) (GR, Merck limited, Worli, Mumbai-400018) was kept over 4Å molecular sieves for about 12-14 hrs and then it was distilled through vertical fractional column. Pure sample of benzene C_6H_6 was dried by freshly cut sodium wires and was kept for about 22-24 hrs and occasional shaking was done. Then benzene was distilled through vertical fractional column. The middle fractions of each distilled solution were collected for use. The X-band microwave bench was used to measure the wavelength in the dielectric medium and 'Voltage Standing Wave Ratio' VSWR using a short-circulating plunger. The experimental set up was tuned at microwave frequency 9.88 GHz. Dielectric permittivity (ε') and dielectric loss (ε'') of dilute solution of acetone in benzene solution was obtained by using Heston *et al* technique⁶. Set of dilute solutions of the acetone and benzene solutions were prepared and all the measurements were made at different temperatures (25, 30, 35 and 40° C) by circulating water around the dielectric cell through a thermostat (LAUDA DR R WOBSEER GMBH & CO. KG German made). The densities and viscosities of the solutions were measured by Ubbelohde viscometer and sealable type of pycnometer, respectively.

RESULTS AND DISCUSSION

The dielectric permittivity (ϵ') and dielectric loss (ϵ'') for the dilute solutions of acetone (CH_3COCH_3) in benzene solution have been calculated, using standing wave techniques and are given in Table 1. Following equations have been used:

$$\epsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \quad \dots(1)$$

$$\epsilon'' = \frac{2}{\pi} \left(\frac{\lambda_0}{\lambda_c}\right)^2 \left(\frac{\lambda_g}{\lambda_d}\right) \left(\frac{d\rho}{dn}\right) \quad \dots(2)$$

Where λ_0 , λ_c , λ_g and λ_d are the wave lengths of microwave in free space, the cut-off wave length, the wave guide wave length, the wave guide wave length in the wave guide filled with solution, respectively. ρ is the inverse of 'Voltage Standing Wave Ratio' (VSWR) and $d\rho/dn$ is the slope of ρ versus n . Here n is the integer ($n = 1, 2, 3\dots$). The relaxation time (τ) and the dipole moment (μ) of the rotating molecular entities have been calculated by the single frequency concentration variational method of Gopala Krishna⁷. This method involves the following basic assumptions:

- (i) The rotating molecular entities are far-far removed from each other so that dipole-dipole interaction could be neglected. The benzene provides the necessary suspension medium for the isolated acetone molecule. This ensures the applicability of Debye theory for dielectric relaxation process.
- (ii) The theory is applicable for dilute solutions of acetone in benzene. The range of dilute solutions should be such that the dielectric permittivity (ϵ') versus weight fraction and dielectric loss (ϵ'') versus weight fraction curves must be linear.

Table 1. Dielectric permittivity (ϵ'), dielectric loss (ϵ''), relaxation time (τ) and dipole moment (μ) for acetone in benzene at different temperatures

Temp. (°C)	Weight fraction of solute in benzene (W)	(ϵ') ($\pm 1\%$)	(ϵ'') ($\pm 3\%$)	$\tau/10^{-12}$ (sec)	μ (D)
25	0.0100	2.3966	0.0233	2.28	2.79
	0.0110	2.4136	0.0253		

Temp. (°C)	Weight fraction of solute in benzene (W)	(ϵ') ($\pm 1\%$)	(ϵ'') ($\pm 3\%$)	$\tau/10^{-12}$ (sec)	μ (D)
30	0.0137	2.4548	0.0324	2.12	2.79
	0.0160	2.4834	0.0375		
	0.0176	2.5057	0.0414		
	0.0100	2.3906	0.0219		
	0.0110	2.4051	0.0240		
	0.0137	2.4461	0.0297		
	0.0160	2.4814	0.0349		
	0.0176	2.5057	0.0386		
35	0.0100	2.3670	0.0203	1.98	2.79
	0.0110	2.3817	0.0218		
	0.0137	2.4211	0.0274		
	0.0160	2.4550	0.0318		
	0.0176	2.4795	0.0355		
40	0.0100	2.3480	0.0199	1.82	2.79
	0.0110	2.3625	0.0216		
	0.0137	2.3989	0.0256		
	0.0160	2.4335	0.0302		
	0.0176	2.4571	0.0338		

- (i) The method gives the average value of the relaxation time (τ). This could be taken as the macroscopic relaxation time (τ). The relaxation time (τ) and dipole moment (μ) have been calculated by the following equations:

$$\tau = \frac{1}{\omega} \left[\frac{dy}{dx} \right] \quad \dots(3)$$

$$\mu^2 = \frac{9KTM}{4\pi N d_0} \left(1 + \left[\frac{dy}{dx} \right]^2 \right) \frac{dx}{dW} \quad \dots(4)$$

Where,

$$x = \frac{\epsilon'(\epsilon' + 1) + \epsilon''^2 - 2}{(\epsilon' + 2)^2 + \epsilon''^2} \quad \dots(5)$$

$$y = \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} \quad \dots(6)$$

Where d_0 is the density of the solvent (benzene); M is the molecular weight; W is the weight fraction of the acetone in the solution; K is the Boltzmann's constant; T is the absolute temperature and N is the Avogadro's number. The ε' and ε'' values were estimated to be reproducible within $\pm 1\%$ and $\pm 3\%$, respectively. The curves of ε' and ε'' versus weight fraction of acetone in benzene solution are found to be linear (Fig. 1 and Fig. 2) at 25°C . The linear variations of ε' , ε'' ensures the applicability of Debye's theory⁸ and hence, that of Gopala Krishna's method for calculating relaxation time and dipole moment of acetone in non-polar solvent benzene.

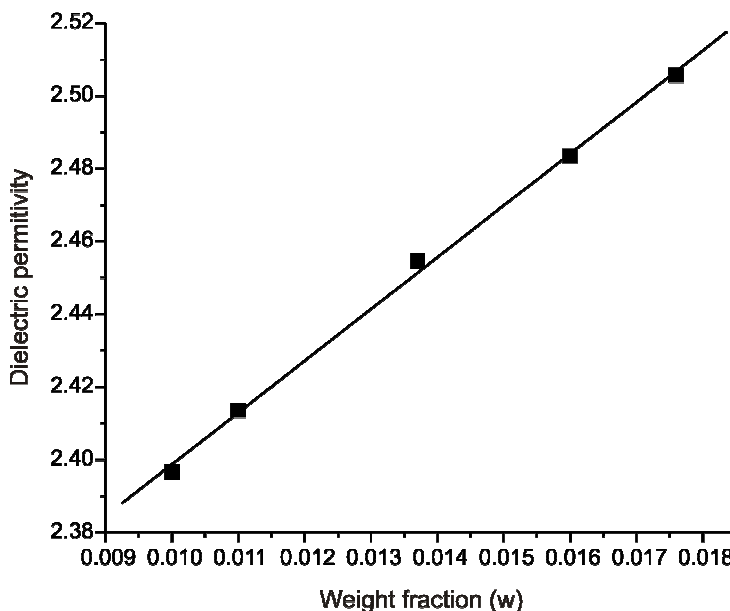


Fig. 1: Variation of dielectric permittivity with weight fraction (W)

The values of ε' , ε'' , τ and μ thus determined from microwave absorption data are shown in Table 1. It is found that dielectric relaxation time (τ) decreases with rise in temperature. This behavior may be explained on the bases of Debye's theory of dielectric relaxation⁸. The variations of $\log(\tau T)$ versus $10^3/T$ (Fig. 3) and $\log(\eta)$ versus $10^3/T$ are found to vary linearly. This indicates that the dielectric relaxation process may be treated as the activated process.

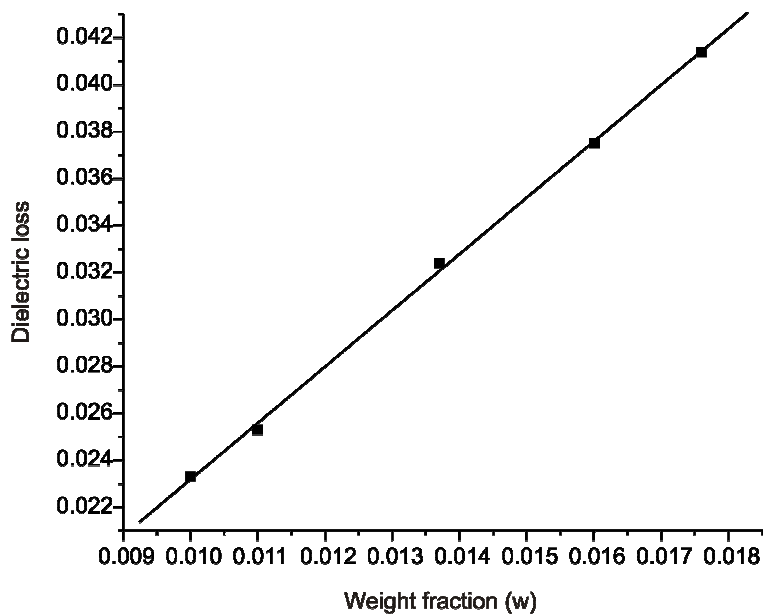


Fig. 2: Variation of dielectric loss with weight fraction (W)

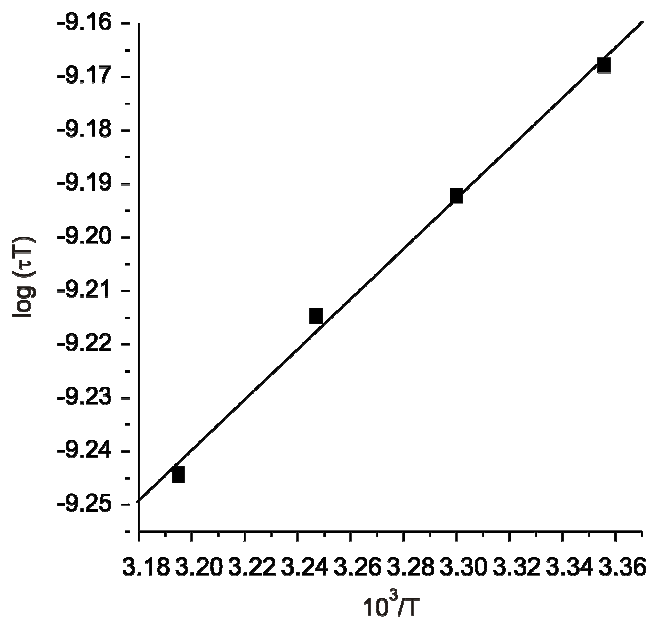


Fig. 3: Plot between $\log(\tau T)$ versus $10^3/T$ of acetone (CH_3COCH_3) in benzene solution

Energy parameters (ΔH_ϵ , ΔF_ϵ , ΔS_ϵ) for dielectric relaxation process of acetone in benzene solutions and corresponding energy parameters (ΔH_η , ΔF_η , ΔS_η) for the viscous flow of benzene have been calculated and compared at different temperatures (25, 30, 35 and 40° C) by using the Eyring rate relations⁹. Slope= $\Delta H/2.303R$.

Dipole moment of acetone in benzene solution is found to be very close to the literature value of unassociated acetone molecule ($\mu = 2.80$ D). This shows that acetone exists in monomer form in benzene solution. It is interesting to note that in benzene solution, the dipole moment of acetone do not vary with rise in temperature.

Table 2: Enthalpies of activation (ΔH_ϵ , ΔH_η in kcal mol⁻¹), free energy of activation (ΔF_ϵ , ΔF_η in kcal mol⁻¹), entropies of activation (ΔS_ϵ , ΔS_η in cal mol⁻¹ deg k⁻¹) for acetone (CH₃COCH₃) in benzene solution at different temperatures

T (°C)	$\tau/10^{-12}$ (sec ⁻¹)	ΔH_ϵ	ΔF_ϵ	ΔS_ϵ	ΔH_η	ΔF_η	ΔS_η
25	2.280	2.143	1.564	1.944	2.615	2.917	-1.012
30	2.120	2.143	1.556	1.939	2.615	2.923	-1.018
35	1.980	2.143	1.550	1.927	2.615	2.930	-1.018
40	1.820	2.143	1.533	1.950	2.615	2.945	-1.018

The non-variation of dipole moment of acetone in benzene solution predicts that there is no possible solute-solvent type of molecular association in the solution with the increasing temperature. The energy parameters for the dielectric relaxation process (ΔH_ϵ , ΔF_ϵ , ΔS_ϵ) and for the viscous flow process (ΔH_η , ΔF_η , ΔS_η) are given in the Table 2.

It is found that the enthalpy of activation for the dielectric relaxation process (ΔH_ϵ) is less than the enthalpy of the viscous flow process (ΔH_η). The enthalpy of activation depends upon the local environment of the molecules. Different values for the enthalpy of activation indicate that the dielectric process and viscous flow process involve the breaking of bonds with the neighboring molecules in a different way and to a different extent. 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 bases that the dielectric relaxation process involves the rotation of molecular entities where as in the flow process, the rotational as well as the translational motion of the molecules is involved. The entropy of the 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 becomes –ve where as +ve value of the change in the entropy for activated process indicates the non-cooperative environment of the system and the activated state is unstable. In the present case, it is observed that the change in entropy of the dielectric relaxation process is +ve, indicating that the environment of the system is non-cooperative and unstable, like the activated viscous flow state.

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