



Microwave Dielectric Study of Tetramethylurea and *N, N*-Dimethylacetamide Binary Mixture in Benzene

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Abstract: Dielectric relaxation of the binary mixture of tetramethylurea and *N, N*-dimethylacetamide has been studied at fixed frequency and temperature (9.88 GHz & 298 K respectively) in benzene solution. Different dielectric parameters like the dielectric constant (ϵ') and the dielectric loss (ϵ'') at microwave frequency, static dielectric constant (ϵ_0) and dielectric constant (ϵ_∞) at optical frequency were determined. The values of relaxation time ($\tau_{(1)}$, $\tau_{(2)}$, $\tau_{(0)}$ & τ_{GK}) have been calculated using Higasi's single frequency method and Gopala Krishna's method. Using Eyring's rate theory, the activation energies for the process of dielectric relaxation and viscous flow were calculated and compared. The study of dielectric properties of the binary mixture reveals the existence of the solute-solute type of molecular associations.

Keywords: Tetramethylurea (TMU), *N, N*-Dimethylacetamide (DMA), Binary mixture, Microwave absorption, Dielectric relaxation

Introduction

The interaction of electrical energy with matter is determined by the electromagnetic properties of the material. On a macroscopic scale under steady state conditions, these properties are permittivity and permeability of material. Dielectric studies are of great help in the assignment of the molecular structures or configurations, particularly those of organic compounds¹⁻³. Although IR and NMR studies are powerful tools for studying intermolecular *H*-bonds, dielectric studies provide very useful information about molecular dynamics and other intrinsic and extrinsic properties related to the molecular systems⁴⁻⁷. The dielectric relaxation behavior has been extensively studied with varying emphasis by various workers⁸⁻¹².

Amides form the basic building block in proteins; therefore, the dielectric studies of binary mixtures of amides are expected to be of great interest. Binary mixtures of amides

have been studied and reported by number of research workers. Recently the dielectric relaxation mechanism of dilute solutions of amides was studied by malathi¹³ and solute-solute type of molecular associations was proposed. Dielectric relaxation behavior of binary mixtures of DMF + TMU and DMA + DMF was studied by Chatterjee *et al*¹⁴ and the binary mixture of NMA + DMA in benzene solution by Kumar *et al*¹⁵. However no information is available about the dielectric relaxation mechanism of the binary mixture of tetramethylurea and *N, N*-dimethylacetamide. In the present investigation the dielectric relaxation properties of the binary mixtures of tetramethylurea and *N, N*-dimethylacetamide in benzene solution at 298 K using 9.88 GHz frequency have been studied. *N, N*-dimethylacetamide is a non-aqueous solvent with dielectric constant (ϵ') = 37.78 and dipole moment $\mu = 3.79\text{D}$ ¹⁶. *N, N*-dimethylacetamide is used as solvent for chloromycin racemate and the effects on blood pressure and respiration studies. Tetramethylurea is a non-aqueous solvent with the dielectric constant (ϵ') = 23.45 ± 0.06 and the dipole moment $\mu = 3.37\text{D}$ ¹⁷. The combination of high dipole moment, moderate relative permittivity, low viscosity and low specific conductance, makes tetramethylurea a useful solvent for studying the behaviour of electrolytes in solution¹⁷. The pure tetramethylurea has been studied experimentally and many of its physico chemical properties are available in the literature¹⁸.

It is possible to prepare binary mixtures of tetramethylurea and *N, N*-dimethylacetamide having dielectric constants values in between those of tetramethylurea and *N, N*-dimethylacetamide. Tetramethylurea and *N, N*-dimethylacetamide has quite different dielectric constants but exhibit similar values for the dipole moments. This motivated the authors to perform experimental study concerned with the dielectric relaxation process in binary mixtures of tetramethylurea and *N, N*-dimethylacetamide in order to understand the molecular association in the whole concentration range of tetramethylurea in the binary mixture.

Measurements of dielectric constant (ϵ'), dielectric loss (ϵ''), static dielectric constant (ϵ), dielectric constant at optical frequency (ϵ_∞), distribution parameter (α), dielectric relaxation times ($\tau_{(1)}$, $\tau_{(2)}$, $\tau_{(0)}$ & τ_{GK}) and dipole moment (μ) have been made for binary mixtures with different mole fractions of tetramethylurea (0.00, 0.20, 0.40, 0.50, 0.60, 0.80, and 1.00) in the mixture at 298 K. The plots of dielectric relaxation time versus the mole fraction of tetramethylurea in the binary mixtures propose solute-solute associations.

Experimental

N, N-Dimethylacetamide [central Drug House (p) Ltd., Mumbai] was kept over 4 Å molecular sieves for 48 h and then distilled through long vertical fractionating column. Benzene (GR grade) from E. Merck Ltd. (Mumbai India) was dried by refluxing over freshly cut sodium metal and then distilled through a long vertical fractionating column. Tetramethylurea (Fluka) was dried over anhydrous BaO powder for 48 h and then it was distilled through a long vertical fractionating column. The middle fraction of each solution was collected for use.

The functional block diagram of the x-band microwave bench used in the present investigation for the measurement of the dielectric constant and the dielectric loss at 9.88 GHz frequency is shown in Figure 1. Microwaves produced by klystron are passed through an isolator, screw tuner, variable attenuator, frequency meter, slotted line section fitted with a tunable traveling probe and a 1 N 23 B crystal detector, *E*-plane bend and dielectric cell. The microwave bench was used to measure the voltage standing wave ratio (VSWR), the wavelength of microwaves in the waveguide (λ_g), in the dielectric (λ_d) in the free space (λ_0) and the cutoff wavelength (λ_c). Heston *et al*¹⁹ method adopted for short circuited terminations

was used to calculate the dielectric constant and dielectric loss. The accuracy in the measurement of ϵ' and ϵ'' is about $\pm 1\%$ and $\pm 5\%$ respectively. The static dielectric constant (ϵ_0) was measured at the frequency 2 MHz by "WTW Dipolemeter DM01" (uncertainty better than $\pm 1\%$) based on the principle of heterodyne beat method. An abbe refractometer was used to measure refractive index n_D of the sodium D-line for the investigated solutions with an error about $\pm 1.1 \times 10^{-4}$. The square of the refractive index gave the value of optical permittivity ($\epsilon_\infty = n_D^2$).

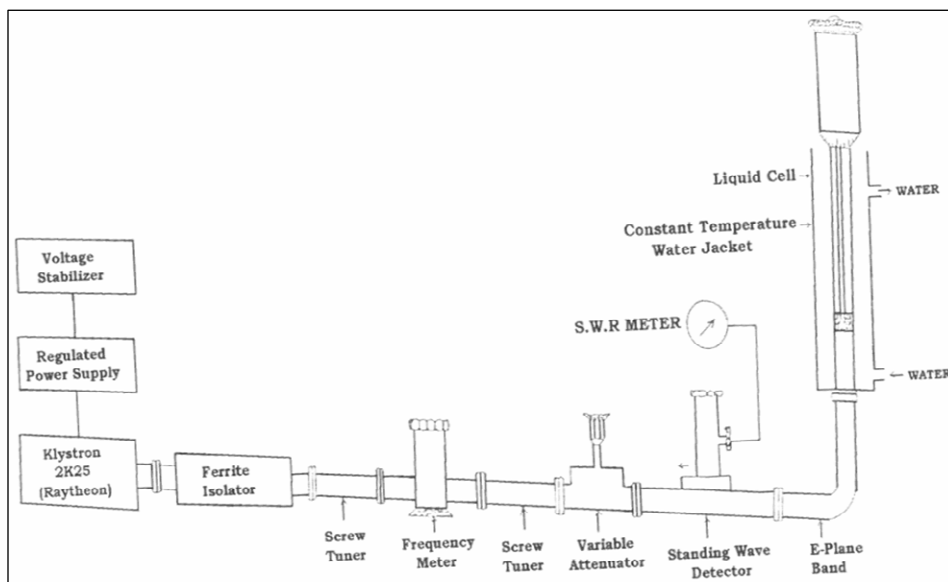


Figure 1. Schematic arrangement of x-band microwave test bench

All the measurements were made at a fixed temperature of 298 K. Thermostat with a water bath was used to circulate water around the dielectric cell to maintain a constant temperature within accuracy limit of ± 0.05 °C. The viscosities and densities of the solutions were measured by an Ubbelohde viscometer and a sealable type of pycnometer, respectively.

Results and Discussion

The dielectric constant of the mixture is measured using Rodert and Von Hippel's method²⁰. The shift of the first minima of standing wave pattern produced by a short circuit in the space in front of the sample depends upon the wavelength of the electromagnetic wave in the dielectric material and hence is related to the dielectric permittivity (ϵ') of the material. The phase constant along the axis of a hollow waveguide of uniform cross-section and highly conducting walls, is given by

$$\gamma_d = \frac{2\pi j}{\lambda_o} \left[\epsilon^* - \left(\frac{\lambda_o}{\lambda_c} \right)^2 \right]^{\frac{1}{2}} \quad (1)$$

Where $\epsilon^* = \epsilon' - j\epsilon''$, λ_o is the free space wavelength and λ_c cutoff wavelength. Separating the real and imaginary parts of ϵ^* we get

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

$$\epsilon'' = \frac{2}{\pi} \left(\frac{\lambda_0}{\lambda_d} \right)^2 \frac{\lambda_g}{\lambda_d} \frac{d\rho}{dn} \quad (3)$$

Here λ_g , λ_d and ρ are the waveguide wavelength, the wavelength in the waveguide filled with the dielectric and the inverse of the voltage standing wave ratio respectively. $\frac{d\rho}{dn}$ is the slope of the curve of ρ versus n . Here n is an integer ($n=1,2,3,\dots$), such that $\left(\frac{n\lambda_d}{2} \right)$ represents the length of the dielectric filled waveguide.

According to Heston *et al*¹⁹ the dielectric constant and dielectric loss for dilute solutions of polar solute in non-polar solvent are proportional to solute weight fraction. The linear relationship is represented by the following equations.

$$\begin{aligned} \epsilon' &= \epsilon_1 + a'w_2 \\ \epsilon'' &= a''w_2 \\ \epsilon_0 &= \epsilon_{10} + a_0w_2 \\ \epsilon_\infty &= \epsilon_{1\infty} + a_\infty w_2 \end{aligned} \quad (4)$$

Where the subscripts 1 and 2 refer to the non polar solvent and the polar solute respectively and the subscripts 0 and ∞ refer to the static frequency and the optical frequency respectively and w_2 is the weight fraction of the solute. The coefficients a' , a'' , a_0 and a_∞ are the slopes obtained from the linear plots of ϵ' , ϵ'' , ϵ_0 and ϵ_∞ versus weight fractions (w_2) respectively. The average relaxation time (τ_0) and distribution parameter (α) were calculated using Higasi's²¹ single frequency measurement equations:

$$\tau_0 = \frac{1}{\omega} \left(\frac{A^2 + B^2}{C^2} \right)^{\frac{1}{2(1-\alpha)}} \quad (5)$$

$$1 - \alpha = \frac{2}{\pi} \tan^{-1} \left(\frac{A}{B} \right) \quad (6)$$

Where $A = a''(a_0 - a_\infty)$, $B = (a_0 - a')(a' - a_\infty) - a''^2$, $C = (a' - a_\infty)^2 + a''^2$ and ω is the angular frequency. The relaxation time corresponding to group rotation $\tau_{(1)}$ and segmental reorientation $\tau_{(2)}$ were calculated using the equations of Higasi *et al*²² proposed for dilute solutions.

$$\tau_{(1)} = \frac{a''}{\omega(a' - a_\infty)} \quad (7)$$

$$\tau_{(2)} = \frac{(a_0 - a')}{\omega a''} \quad (8)$$

Relaxation time (τ_{GK}) has also been determined by Gopala Krishna's method²³. In this

method the dielectric constant and dielectric loss were determined at a single frequency. A graph is plotted between two parameters X and Y , which are given by the following equations:

$$X = \frac{\epsilon'^2 + \epsilon''^2 + \epsilon' - 2}{(\epsilon' + 2)^2 + \epsilon''^2} \quad (9)$$

$$Y = \frac{3\epsilon''}{(\epsilon' + 2)^2 + \epsilon''^2} \quad (10)$$

$$\tau = \frac{\lambda_0}{2\pi c} \left(\frac{dY}{dX} \right) \quad (11)$$

Here X and Y are intermediate parameters which depend upon ϵ' and ϵ'' . Gopala Krishna's method²³ has also been used to calculate the dipole moment of the polar solutes and their binary mixtures. The equation used is:

$$\mu^2 = \frac{9kTM}{4\pi Nd} \left[1 + \left(\frac{dY}{dX} \right)^2 \right] \frac{dX}{dW} \quad (12)$$

Where k is the Boltzmann's constant, T is absolute temperature of the system, N the avogadro number, M the molecular weight of the solute and d is the density of the solvent. The values of Higasi's dielectric relaxation times ($\tau_{(1)}$, $\tau_{(2)}$, $\tau_{(0)}$), Gopala Krishna's relaxation time (τ_{GK}) and the dipole moment (μ) for binary mixtures of different mole-fractions of tetramethylurea (0.00, 0.20, 0.40, 0.50, 0.60, 0.80 and 1.00) at 298 K have been tabulated (Table 1). The molar free energies (ΔF , ΔF_n) for the dielectric relaxation process and the viscous flow process have been calculated using the Eyring's rate equations²⁴ (Table 2).

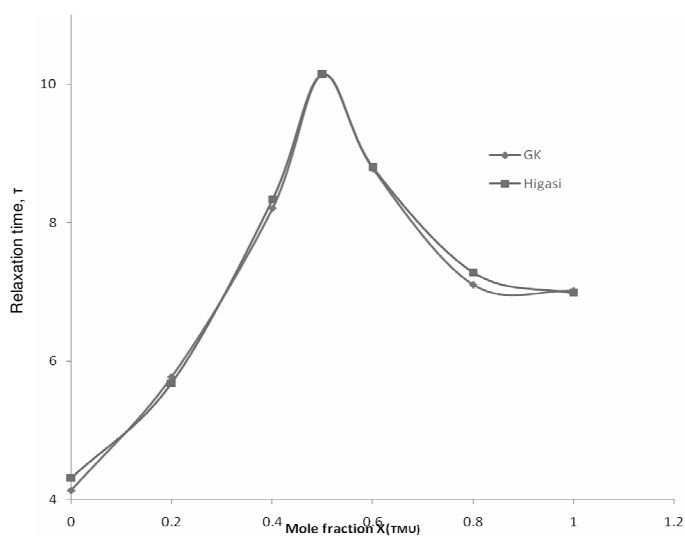
The relaxation time for pure tetramethylurea is found to be more than that of pure N , N -dimethylacetamide. The relaxation time increases with the size of the molecule and may be discussed in terms of the molecular shape and solvent microscopic viscosity. This shows that the size of tetramethylurea molecule is more than N , N -dimethylacetamide molecule. The non-monotonic variation of the dielectric relaxation time with the mole fraction of tetramethylurea in the binary mixtures was observed (Figure 2). The monotonic variation of the relaxation time, from its value corresponding to one single constituent to the value which corresponds to the other pure constituent, with varying mole fraction in the whole concentration range may be taken as the absence of any solute-solute association in the mixture²⁵. On the other hand the non monotonic variation of the relaxation time with the mole fraction is interpreted as a possible solute-solute molecular association in the binary mixture²⁶. In the present study, the non-monotonic variation of the relaxation time with the change in mole-fraction of tetramethylurea in the binary mixture was observed. The relaxation time increases sharply with the increase in mole-fraction from 0.0 to 0.5.

The peak is formed at 0.5 mole-fraction of tetramethylurea in the binary solution and the relaxation time attains maximum value at this mole-fraction. With the further increase in the mole fraction of tetramethylurea in the mixture there is a decrease in the relaxation time and falls towards the value of pure tetramethylurea in the benzene solution. This predicts the solute-solute type of molecular association between tetramethylurea and N , N -dimethylacetamide. The solute-solute type of molecular association may arise because of dipole-dipole

Mole fraction	W_2	ϵ_0	ϵ'	ϵ''	ϵ_∞	α	Higasi's Relaxation time (ps)			GK (ps)	Dipole Moment(D)
							$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$	τ_{GK}	μ
0.00	0.0021	2.410	2.360	0.012	2.320	0.27	2.36	7.86	4.31	4.13	3.55
	0.0040	2.440	2.390	0.019	2.315						
	0.0066	2.490	2.430	0.029	2.310						
	0.0087	2.530	2.460	0.039	2.305						
0.20	0.0024	2.420	2.370	0.008	2.314	0.26	3.49	9.26	5.68	5.77	4.09
	0.0047	2.479	2.410	0.020	2.311						
	0.0066	2.529	2.450	0.037	2.310						
	0.0089	2.581	2.490	0.051	2.307						
0.40	0.0021	2.435	2.390	0.007	2.315	0.29	5.18	13.44	8.34	8.21	3.96
	0.0044	2.480	2.420	0.021	2.312						
	0.0062	2.550	2.450	0.038	2.310						
	0.0084	2.585	2.480	0.056	2.309						
0.50	0.0026	2.450	2.425	0.008	2.320	0.28	6.40	16.07	10.14	10.14	3.84
	0.0048	2.490	2.445	0.019	2.319						
	0.0067	2.550	2.470	0.039	2.318						
	0.0084	2.590	2.495	0.053	2.317						
0.60	0.0032	2.445	2.410	0.009	2.320	0.27	5.62	13.79	8.80	8.78	3.68
	0.0056	2.490	2.435	0.020	2.319						
	0.0078	2.545	2.460	0.036	2.318						
	0.0097	2.575	2.485	0.052	2.317						
0.80	0.0030	2.450	2.400	0.011	2.321	0.25	4.77	11.13	7.28	7.10	3.80
	0.0052	2.490	2.415	0.020	2.320						
	0.0073	2.530	2.445	0.035	2.319						
	0.0095	2.575	2.480	0.050	2.318						
1.00	0.0020	2.440	2.390	0.009	2.322	0.28	4.28	11.38	6.98	6.83	3.16
	0.0042	2.470	2.410	0.019	2.321						
	0.0069	2.500	2.430	0.027	2.320						
	0.0091	2.530	2.450	0.036	2.319						

Table 2. The activation energies (ΔF_η , ΔF_τ) of the binary mixture (TMU + DMA) in benzene at 298 K

Mole fraction	W_2	Activation energy	
		ΔF_η k.J/mol	ΔF_τ k.J/mol
0.00	0.0021	2.46	1.95
	0.0040		
	0.0066		
	0.0087		
0.20	0.0024	2.61	2.11
	0.0047		
	0.0066		
	0.0089		
0.40	0.0021	2.87	2.34
	0.0044		
	0.0062		
	0.0084		
0.50	0.0026	2.98	2.46
	0.0048		
	0.0067		
	0.0084		
0.60	0.0032	2.88	2.37
	0.0056		
	0.0078		
	0.0097		
0.80	0.0030	2.80	2.26
	0.0052		
	0.0073		
	0.0095		
1.00	0.0020	2.74	2.23
	0.0042		
	0.0069		
	0.0091		

**Figure 2.** The variation of the relaxation times (τ_{GK} & τ_{Higasi}) with the mole fraction $X_{(TMU)}$ of tetramethylurea in the binary mixture (TMU + DMA) in benzene at 298 K

A finite and significantly high value of distribution parameter indicates existence of more than one relaxation processes. Non-zero values of α are obtained for dilute solutions of the binary mixture in benzene, which indicates that there is a large contribution of segment reorientation and group rotation to the relaxation processes, besides the overall rotation. This is further confirmed by the different values of $\tau_{(1)}$ and $\tau_{(2)}$ and indicates the existence of an intramolecular relaxation process in addition to the overall relaxation process. Davidson *et al.*²⁷ have shown that resolution of the relaxation times into intramolecular contribution $\tau_{(1)}$ and intermolecular contribution $\tau_{(2)}$ is possible only if the ratio of the two relaxation times is greater than 6. In the present study the ratio is of the order of 3, hence further resolution is not possible.

The calculated dipole moments of tetramethylurea and *N, N*-dimethylacetamide were found to be very near to the literature values. This shows that pure *N, N*-dimethylacetamide and pure tetramethylurea exist in the monomer form in benzene solution. Dipole moment of the molecular entities depends on the size, structure and charge separation in the molecular entities.

The free energy of activation for dielectric relaxation ΔF and viscous flow ΔF_η has been tabulated (Table 2). The molar free energy of activation for viscous flow is greater than the free energy of activation for dielectric relaxation. This is due to the fact that the viscous flow process involves both the rotational and translational motion of the molecular entities whereas the dielectric relaxation process involves only the rotational motion of the molecules. This confirms the fact that the process of viscous flow involves greater interference by neighbours than does dielectric relaxation. It is further suggested that for non-associated polar liquids the free energy of activation for rotation and for viscous flow would be

$$\Delta F_\epsilon < 0.5\Delta F_\eta$$

In the present case, ΔF is larger than expected. This suggests that, the molecular entities in the mixture can no longer be considered as spherical and the rotation necessarily requires a translational motion of the neighbours.

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