



Investigation of dielectric relaxation in dipolar liquids from conductivity measurement

D KUMAR¹, S K SIT², S N SINGH¹ and S SAHOO^{1,*} 

¹Department of Electronics and Communication Engineering, National Institute of Technology Jamshedpur, Jamshedpur 831014, India

²Department of Physics, Dr. MeghnadSaha Institute of Technology, Haldia 721657, India

*Author for correspondence (swagatdebmsit@yahoo.co.in)

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Abstract. Conductivity (σ_{ijk} 's) measurement method is proposed to investigate dielectric relaxation in ternary polar–nonpolar mixture of *N,N*-dimethyl formamide (DMF)(j) with pyridine(k) or acetonitrile(k) dissolved in p-xylene (i) at various weight fractions (w_{jk} 's) and temperature under different bands (S, C, X and Ku) of microwave field applying Debye's dielectric model. Ratio of slopes of imaginary σ_{ijk}'' vs. w_{jk} with real σ_{ijk}' vs. w_{jk} of complex conductivity σ_{ijk}^* as well as linear slope of σ_{ijk}'' vs. σ_{ijk}' are used to predict τ_{jk} 's (relaxation time) and μ_{jk} 's (dipole moments). Various molecular associations are also identified from the meaningful interactions among polar–nonpolar molecules in terms of τ_{jk} and μ_{jk} . Molecular dynamics or molecular environment surrounding the polar molecules DMF, pyridine or acetonitrile is extensively studied with the help of estimated thermodynamic energy parameters. The existence of Debye relaxation mechanism in polar–nonpolar mixture is authenticated by the estimated Debye factor. Microwave sensor development is also ascertained from various dielectric parameters like permittivity, conductivity and penetration depth under microwave field.

Keywords. Conductivity; relaxation time; dipole moment; penetration depth; dielectric relaxation.

1. Introduction

The precise and reliable information of different solute–solute, solute–solvent and self-molecular association can be gained effortlessly with the help of the Debye dielectric relaxation method for the combination of polar–nonpolar liquid mixture [1,2]. Since microwave has the tendency to identify weaker molecular association, the monomer as well as dimers can be detected easily in the microwave domain [3]. *N,N*-dimethyl formamide (DMF) having small evaporation rate is extensively utilized as solvent in peptide coupling in pharmaceuticals, progression and manufacturing of surface coatings, synthetic leathers, adhesives, pesticides, films, fibres as well as in electro spinning. DMF is efficient in isolating and suspending carbon nanotubes, and as suggested by the NIST for use in near-infrared spectroscopy and also as a standard in proton NMR spectroscopy permitting for a quantitative measurement of an unidentified compound. DMF is a necessary constituent of enzymes and proteins [4,5]. Acetonitrile is anachromatic liquid and it is an elementary organic nitrile. It is commonly used solvent in refineries for distillation of butadiene. In battery industry, acetonitrile is extensively used due to its ability to dissolve electrolytes of high dielectric constant. Acetonitrile also acts as an important solvent in the

manufacture of DNA oligonucleotides from monomers, pharmaceuticals and photographic film. Pyridine is a useful solvent for various organic liquids and incorporated in wide variety of reactions, such as oxidation, reduction, electrophilic and nucleophilic substitution. It is necessary to realize the mutual interaction of DMF with other polar molecules like pyridine and acetonitrile for gathering information on the conformational stability of protein molecules. All the polar molecules (DMF, pyridine and acetonitrile) are non-aqueous aprotic solvents showing high dielectric constant and dipole moments. The molecular aspect of DMF, pyridine and acetonitrile motivated us to investigate the dielectric relaxation characteristics of binary mixture of the said materials. Several polar groups dominate in each of polar liquid mixture, where inductive, mesomeric and electromeric effects are extremely significant to properly understand the molecular interaction. Previously, conductivity measurement method has been properly utilized in the mixture of polar and nonpolar liquid in radio and microwave electric fields [6,7]. Earlier, study of DMF + pyridine mixture was undertaken at different temperatures under X-band (9.875 GHz) microwave region [8] using conductivity measurement technique. However, no such detailed investigation from conductivity measurement method on the dual polar combination of amide and a



Figure 1. (a) Network analyzer assembly and (b) coaxial probe with flange.

heterocyclic ring compound mixed in nonpolar solvent p-xylene under broadband electric field is made so far. The aim of this research paper is to know the characteristics collaboration among the aliphatic as well as the heterocyclic ring compound from calculated parameters. Restricted molecular charge of the polar molecules is dealt with the conductivity measurement method in higher frequency (GHz), while all kind of polarization is involved with the permittivity measurement method. The Debye model in higher frequency and static electric field signifies the collaboration of liquid mixture of polar and nonpolar solvents in diluted solution at molecule level [9,10]. The mixture of the polar and nonpolar solvents absorbs the electric energy vigorously to produce the molecular interactions of monomer (solute–solvent) and dimer (solute–solute) in the microwave region [11,12]. In the this paper, dielectric relaxation study of the diluted solutions of DMF + pyridine or DMF + acetonitrile mixtures in p-xylene have been attempted to acquire sufficient knowledge of dielectric constants, dipole moments, relaxation time and other dielectric relaxation properties to explore the degree of molecular interactions, physico-chemical characteristics and solubility characteristics of polar mixture. The higher dielectric constant of the solvent aids in disintegration of the ions, whereas the molecular orientation of solute–solvent is figured out with the help of dipole moment. Electrostatic factor [13], the result of product of dipole moment and dielectric constant has been successfully applied in determining solvent power of materials. The focus of the current work is to examine the dielectric pattern of DMF(j) with pyridine(k) or acetonitrile(k) mixed in nonpolar solvent p-xylene(i) at 25, 30, 35 and 40°C temperatures, under 3.4 GHz(S-Band), 7.3 GHz(C-Band), 9.8 GHz(X-Band) and 17.2 GHz(Ku-Band) microwave region using conductivity measurement method and Debye dielectric model [14]. The dilute mixture of polar substances in nonpolar solvents helps the solute particle to be tested in a quasi-isolated state and the pattern is influenced in lesser degree by the dipolar

field [10,11]. The Debye [12,14] model is simpler, uncomplicated and quite confined to interpret relaxation study as compared to different standard models. The current study is focused on analytical determination of dielectric behaviour [15] in terms of real $\sigma_{ijk}' (= \omega \epsilon_0 \epsilon_{ijk}'')$, imaginary $\sigma_{ijk}'' (= \omega \epsilon_0 \epsilon_{ijk}')$ parts of higher frequency complex conductivity [16] σ_{ijk}^* of solution under different state of molecular domains.

2. Experimental

The sample DMF, pyridine, acetonitrile and solvent p-xylene are E Merck grade of good quality, were collected from BDH, India, and prior to the use, it was distilled. ϵ_{ijk}' and ϵ_{ijk}'' are appropriately measured with the help of ZNB-20 Vector Network Analyzer (VNA, Rohde & Schwarz made), DAK (dielectric assessment kit) and DAK evaluation software using high temperature probe measurement technique [17], as illustrated in figure 1. The DAK is dipped within the specimen of liquid solution (DMF + pyridine + p-xylene or DMF + acetonitrile + p-xylene). The electromagnetic fields coming out of DAK end permeates through the sample and alters the characteristics. The reflection coefficient, S_{11} (measured reflections) are transformed into dielectric constant data (permittivity, ϵ) using DAK evaluation software. The VNA assembly allows measurement of permittivity up to 20 GHz. Before actual measurement of sample, calibration of DAK is performed using three elements, such as metal shorting block, water as well as air. The accuracy of the calculated ϵ_{ijk}' and ϵ_{ijk}'' of various samples are ± 0.5 and $\pm 1.67\%$, respectively. After simple normalization of permittivity data, real $\sigma_{ijk}' (= \omega \epsilon_0 \epsilon_{ijk}'')$ and imaginary $\sigma_{ijk}'' (= \omega \epsilon_0 \epsilon_{ijk}')$ parts of complex conductivity σ_{ijk}^* at different ω_{jk} 's of solutes were derived and arranged in table 1. The measured ϵ_{ijk} 's and σ_{ijk} 's of solution up to four decimal places are sufficient and relevant to estimate τ and μ using origin programming and

Table 1. Relative permittivities ϵ_{ijk}' , ϵ_{ijk}'' and higher frequency complex conductivity σ_{ijk} , σ_{ijk}' and σ_{ijk}'' of DMF + pyridine or DMF + acetonitrile dissolved in p-xylene at 25, 30, 35 and 40°C temperatures in various microwave field.

System	Frequency (GHz)	Temperature (°C)	Weight fraction	ϵ_{ijk}'	ϵ_{ijk}''	σ_{ijk}'	σ_{ijk}''	σ_{ijk}
(I)DMF + pyridine	3.4	25	0.0035	2.3921	0.0173	0.0033	0.4525	0.4525
			0.0056	2.4252	0.0255	0.0048	0.4587	0.4587
			0.0074	2.4848	0.0384	0.0073	0.4700	0.4701
			0.0093	2.5259	0.0483	0.0091	0.4778	0.4779
		30	0.0035	2.3645	0.0163	0.0031	0.4472	0.4472
			0.0056	2.4069	0.0239	0.0045	0.4553	0.4553
			0.0074	2.4468	0.0355	0.0067	0.4628	0.4628
			0.0093	2.5003	0.0451	0.0085	0.4729	0.4730
		35	0.0035	2.3436	0.0144	0.0027	0.4433	0.4433
			0.0056	2.3805	0.0220	0.0042	0.4503	0.4503
			0.0074	2.4238	0.0337	0.0064	0.4585	0.4585
			0.0093	2.4729	0.0425	0.0080	0.4677	0.4678
		40	0.0035	2.3375	0.0133	0.0025	0.4421	0.4421
			0.0056	2.3758	0.0205	0.0039	0.4494	0.4494
			0.0074	2.4077	0.0318	0.0060	0.4554	0.4554
			0.0093	2.4644	0.0411	0.0078	0.4661	0.4662
	7.3	25	0.0035	2.3842	0.0140	0.0057	0.9682	0.9682
			0.0056	2.4151	0.0222	0.0090	0.9808	0.9808
			0.0074	2.4447	0.0313	0.0127	0.9928	0.9929
			0.0093	2.4757	0.0375	0.0152	1.0054	1.0055
	9.8	25	0.0035	2.3793	0.0124	0.0068	1.2972	1.2972
			0.0056	2.3956	0.0165	0.0090	1.3060	1.3060
			0.0074	2.4210	0.0218	0.0119	1.3199	1.3200
			0.0093	2.4483	0.0275	0.0150	1.3348	1.3349
	17.2	25	0.0035	2.3523	0.0087	0.0083	2.2508	2.2508
			0.0056	2.3682	0.0098	0.0094	2.2660	2.2660
			0.0074	2.3782	0.0107	0.0102	2.2756	2.2756
			0.0093	2.3911	0.0122	0.0117	2.2879	2.2879
(II)DMF + acetonitrile	3.4	25	0.0035	2.3724	0.0351	0.0066	0.4487	0.4487
			0.0056	2.4533	0.0672	0.0127	0.4640	0.4642
			0.0074	2.4841	0.0851	0.0161	0.4699	0.4702
			0.0093	2.5542	0.1053	0.0199	0.4831	0.4835
		30	0.0035	2.3618	0.0333	0.0063	0.4467	0.4467
			0.0056	2.4323	0.0611	0.0116	0.4601	0.4602
			0.0074	2.4732	0.0765	0.0145	0.4678	0.4680
			0.0093	2.5211	0.0905	0.0171	0.4769	0.4772
		35	0.0035	2.3524	0.0285	0.0054	0.4449	0.4449
			0.0056	2.4100	0.0545	0.0103	0.4558	0.4559
			0.0074	2.4515	0.0695	0.0131	0.4637	0.4639
			0.0093	2.5022	0.0782	0.0148	0.4733	0.4735
		40	0.0035	2.3420	0.0263	0.0050	0.4430	0.4430
			0.0056	2.4051	0.0483	0.0091	0.4549	0.4550
			0.0074	2.4312	0.0660	0.0125	0.4599	0.4601
			0.0093	2.4811	0.0742	0.0140	0.4693	0.4695
	7.3	25	0.0035	2.3603	0.0302	0.0123	0.9585	0.9586
			0.0056	2.4342	0.0581	0.0236	0.9885	0.9888
			0.0074	2.4611	0.0766	0.0311	0.9995	1.9999
			0.0093	2.5363	0.0914	0.0371	1.0300	1.0307
	9.8	25	0.0035	2.2892	0.0266	0.0145	1.2480	1.2481
			0.0056	2.3687	0.0477	0.0260	1.2914	1.2917
			0.0074	2.3911	0.0624	0.0340	1.3036	1.3040
			0.0093	2.4785	0.0881	0.0480	1.3512	1.3521
	17.2	25	0.0035	2.2443	0.0202	0.0193	2.1475	2.1476
			0.0056	2.2918	0.0334	0.0320	2.1929	2.1931
			0.0074	2.3220	0.0526	0.0503	2.2218	2.2224
			0.0093	2.3950	0.0714	0.0683	2.2917	2.2927

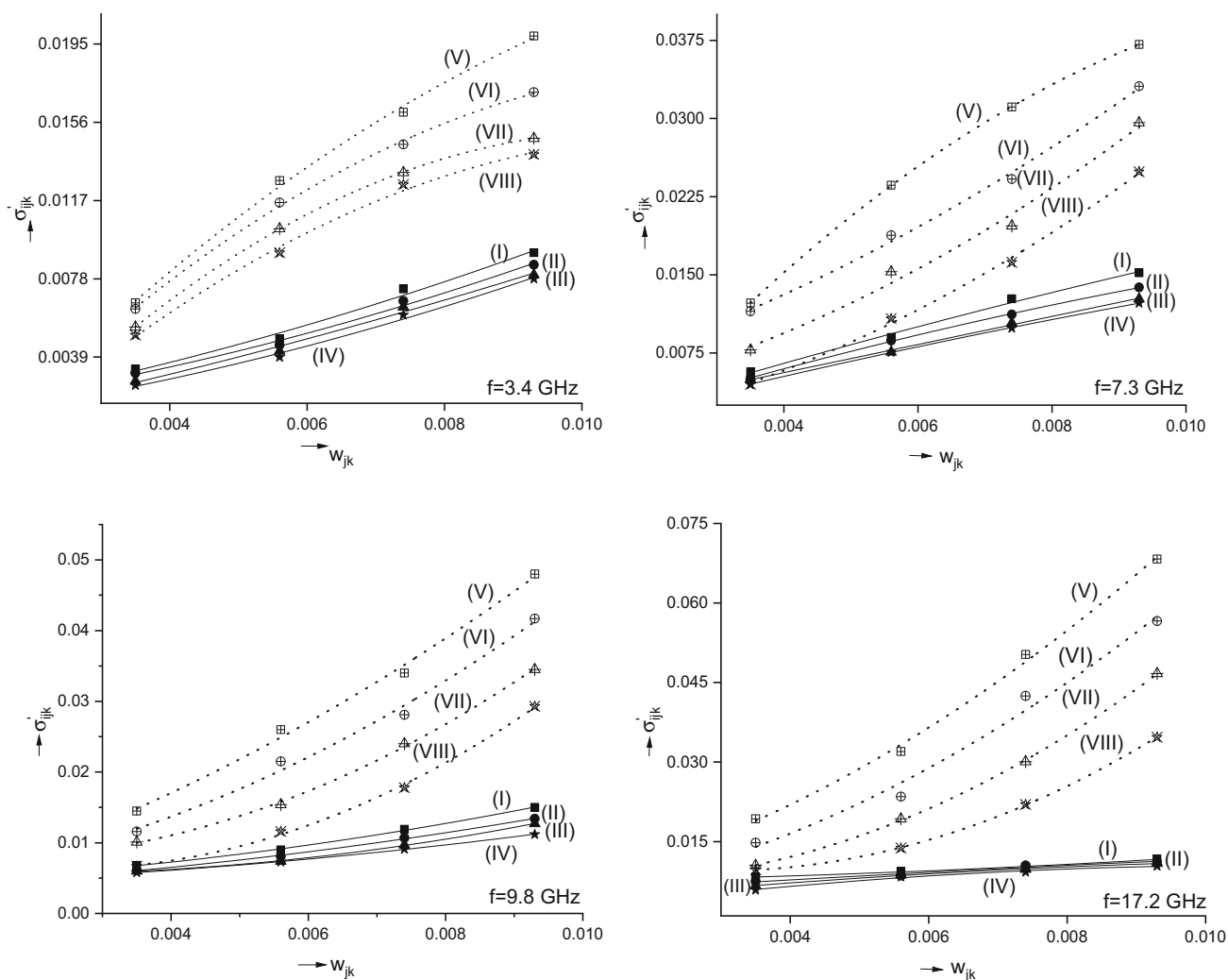


Figure 2. Variations of real part of conductivity σ'_{ijk} against w_{jk} 's of DMF with pyridine or acetonitrile dissolved in p-xylene at different microwave field and temperatures. (I) —■— at 25°C; (II) —●— at 30°C; (III) —▲— at 35°C; (IV) —★— at 40°C for DMF + pyridine, respectively; (V) ...■... at 25°C; (VI) ...●... at 30°C; (VII) ...▲... at 35°C; (VIII) ...★... at 40°C for DMF + acetonitrile, respectively.

least-square fitting procedure. The temperature of the measurement process was adjusted at 25°, 30°, 35° and 40° C with the least count of $\pm 0.1^\circ\text{C}$ with the help of water circulating instrument.

3. Theoretical formulation

3.1 Derivation of relaxation time τ_{jk} from conductivity (σ_{ijk}) measurement

The σ_{ijk}^* [16] due to displacement current of a polar-nonpolar ternary liquid solution (ijk) for a specified w_{jk} 's of solutes is

$$\sigma_{ijk}^* = \sigma'_{ijk} + j\sigma''_{ijk}. \quad (1)$$

where $\sigma_{ijk}' = \omega\epsilon_0\epsilon_{ijk}''$ and $\sigma_{ijk}'' = \omega\epsilon_0\epsilon_{ijk}'$ are the real and imaginary elements of complex conductivity σ_{ijk}^* . ϵ_0 is the absolute permittivity of free space $= 8.854 \times 10^{-12} \text{ F m}^{-1}$. σ_{ijk}' is related to dielectric loss factor ϵ_{ijk}'' and produces intake of heat in the channel. The overall higher frequency complex conductivity σ_{ijk} of the mixture arising due to phase delay between polarization and external electric field:

$$\sigma_{ijk} = \sqrt{(\sigma'_{ijk})^2 + (\sigma''_{ijk})^2}. \quad (2)$$

The σ_{ijk}'' and σ_{ijk}' can be expressed as:

$$\sigma_{ijk}'' = \sigma_{\infty ijk} + \frac{1}{\omega\tau_{ijk}}\sigma'_{ijk}. \quad (3)$$

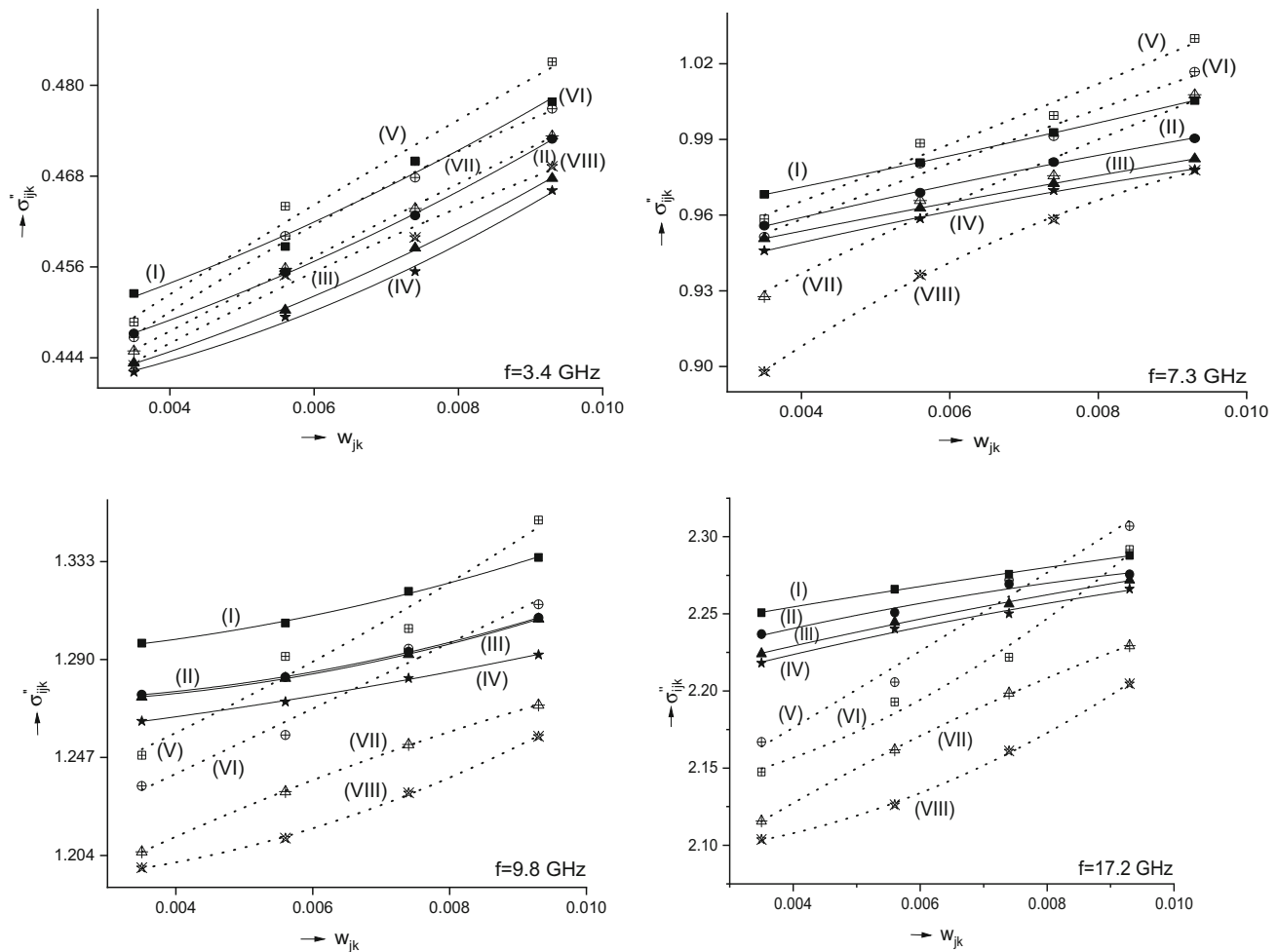


Figure 3. Variations of imaginary part of conductivity σ_{ijk}'' against w_{jk} 's of DMF with pyridine or acetonitrile dissolved in p-xylene at different microwave field and temperatures. (I) \blacksquare at 25°C; (II) \bullet at 30°C; (III) \blacktriangle at 35°C; (IV) \star at 40°C for DMF + pyridine, respectively; (V) \boxplus at 25°C; (VI) \oplus at 30°C; (VII) \boxtimes at 35°C; (VIII) \otimes at 40°C for DMF + acetonitrile, respectively.

Polar-polar interactions can be avoided by formulating τ_{jk} as:

$$\tau_{jk} = \frac{1}{\omega} \frac{\beta_1}{\beta_2}, \quad (4)$$

where β_1 and β_2 are the slopes of σ_{ijk}' vs. w_{jk} and σ_{ijk}'' vs. w_{jk} curves of figures 2 and 3 correspondingly.

On differentiation of equation (3) with respect to σ_{ijk}' , we obtain:

$$\tau_{jk} = \frac{1}{\omega \beta'}, \quad (5)$$

where β' is the slope of σ_{ijk}'' vs. σ_{ijk}' linear relation [18], as depicted in figure 4.

3.2 μ_{jk} (Dipole moment) from σ_{ijk} measurement

The real component σ_{ijk}' of a binary polar-nonpolar liquid solution at $w_{jk} \rightarrow 0$ can be written as [16]:

$$\left(\frac{d\sigma_{ijk}'}{dw_{jk}} \right)_{w_{jk} \rightarrow 0} = \frac{N \rho_i \mu_{jk}^2}{3 M_{jk} K_B T} \frac{\omega^2 \tau_{jk}}{(1 + \omega^2 \tau_{jk}^2)} \frac{(\epsilon_i + 2)^2}{3^2}, \quad (6)$$

where μ_{jk} indicates dipole moment of jk polar mixture, and other nomenclature and denotation carry typical meaning [16]. After simplification of equations (5) and (6), we can get:

$$\mu_{jk} = \left(\frac{27 K_B T M_{jk} \beta}{N \rho_i (\epsilon_{ij} + 2)^2 \omega b} \right)^{1/2}. \quad (7)$$

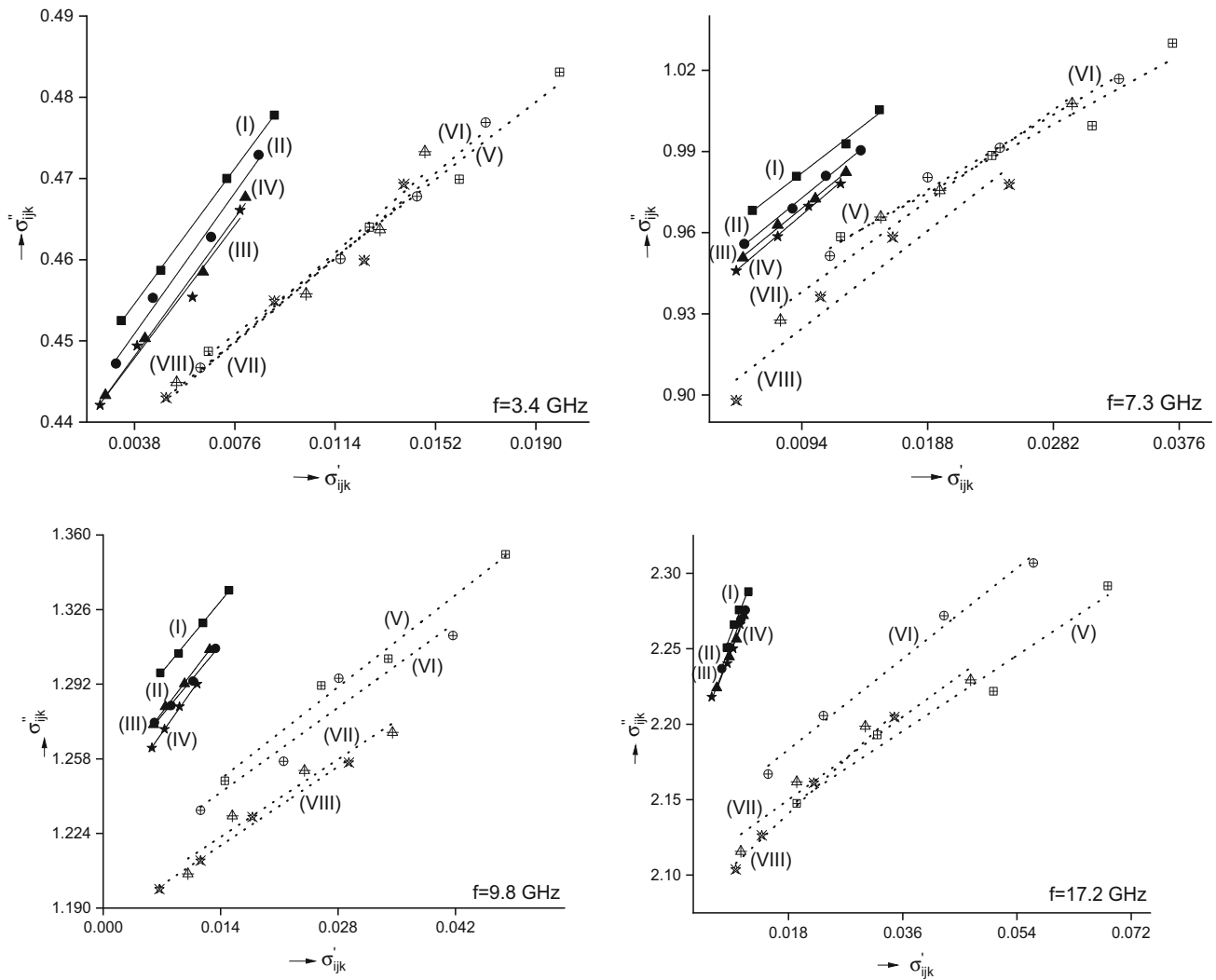


Figure 4. Variations of imaginary part of conductivity σ'_{ijk} against real part of conductivity σ'_{ijk} of DMF with pyridine or acetonitrile dissolved in p-xylene at different microwave field and temperatures. (I) \blacksquare at 25°C; (II) \bullet at 30°C; (III) \blacktriangle at 35°C; (IV) \star at 40°C for DMF + pyridine, respectively; (V) \boxtimes at 25°C; (VI) \oplus at 30°C; (VII) \boxplus at 35°C; (VIII) \star at 40°C for DMF + acetonitrile, respectively.

The denotations utilized in equation (7) signify same interpretations [8,16].

3.3 Penetration depth

The penetration depth, d_p of microwave energy is known as the distance where the energy is decreased to 37%, of its original value at the surface of the element. The value of d_p can be derived [17,19] as:

$$d_p = \frac{c}{2\pi f \sqrt{2\epsilon' \left[\sqrt{1 + \left(\frac{\epsilon''}{\epsilon'} \right)^2} - 1 \right]}}. \quad (8)$$

4. Results and discussion

Measurement of permittivity ϵ_{ijk} 's and conductivity σ_{ijk} 's is performed at various weight fraction w_{jk} 's of DMF + pyridine or DMF + acetonitrile in p-xylene at S-Band(3.4 GHz), C-Band(7.3 GHz), X-Band(9.8 GHz) and Ku-Band (17.2 GHz) microwave field and different temperatures (25, 30, 35, 40°C), as depicted in table 1. Conductivity measurement method [8,16] is applied to derive τ_{jk} 's from the ratio of slopes of σ_{ijk}' vs. w_{jk} and σ_{ijk}'' vs. w_{jk} curves, in figures 2 and 3, individually. The weight fraction w_{jk} 's of dual polar mixture in solution is made extremely dilute and taken up to 4 decimal places, so that solute molecules are sufficiently far apart from each other having no dipole-

Table 2. τ_{jk} from ratio of slopes of σ_{ijk}'' vs. w_{jk} and σ_{ijk}' vs. w_{jk} curve of equation (4), linear slope of σ_{ijk}'' vs. σ_{ijk}' curve of equation (5), reported values from Gopalakrishna (GK) method of binary mixture of DMF and pyridine or acetonitrile dissolved in p-xylene at 25, 30, 35 and 40°C temperatures in various microwave field.

System	Frequency	Temperature	Measured τ (ps) from σ_{ij} measurement		Reported τ (ps) from GK method
			Ratio of slopes of σ_{ijk}'' vs. w_{jk} and σ_{ijk}' vs. w_{jk} curve equation (4)	Linear slope of σ_{ijk}'' vs. σ_{ijk}' curve equation (5)	
(I)DMF + pyridine	3.4	25	6.97	7.02	
		30	6.65	6.76	
		35	6.42	6.54	
		40	6.03	6.11	
	7.3	25	5.78	5.87	
		30	5.55	5.69	
		35	5.33	5.40	
		40	5.10	5.15	
	9.8	25	4.89	4.96	4.46
		30	4.64	4.71	4.23
		35	4.39	4.44	3.98
		40	3.87	3.90	2.82
	17.2	25	3.38	3.42	
		30	3.27	3.35	
		35	3.16	3.20	
		40	3.03	3.10	
(II)DMF + acetonitrile	3.4	25	9.79	9.83	
		30	9.53	9.70	
		35	9.31	9.46	
		40	9.16	9.22	
	7.3	25	8.63	8.70	
		30	8.50	8.59	
		35	8.31	8.44	
		40	8.12	8.22	
	9.8	25	7.88	7.94	7.23
		30	7.50	7.56	6.94
		35	7.34	7.39	
		40	7.14	7.20	
	17.2	25	6.49	6.55	
		30	6.23	6.33	
		35	6.19	6.21	
		40	6.02	6.10	

dipole interaction as demanded by Debye model. The estimated and measured τ_{jk} 's from σ_{ijk}'' vs. σ_{ijk}' linear relation of figure 4 using Murthy *et al* [18] method are listed in table 2 and significantly match with reported values from Gopalakrishna method [20]. The fitted curves indicate that the values of correlation coefficient r 's are nearer to unity $-1 \leq r \leq 1$, demanding sharp correlation between variables. All the graphs in figure 3 show parabolic nature, signifying the solute–solute (dimer) molecular association in the larger concentration domain. The curves in figure 3 are not meeting at a point in the range of $w_{jk} \rightarrow 0$ may be because of

solute–solvent (monomer) association [19]. The variation of σ_{ijk}'' against σ_{ijk}' in figure 4 at different w_{jk} 's and temperatures exhibit linear behaviour ($-1 \leq r \leq 1$), whereas data values are slightly deviated at 40°C in 3.4 GHz for DMF + pyridine solution and at 40°C under 3.4, 7.3 GHz, at 35°C under 7.3 GHz, at 25°C under 17.2 GHz for DMF + acetonitrile mixture. This may happen because of uncertainty in accurate measurement [16]. All the curves of σ_{ijk}'' and σ_{ijk}' against w_{jk} 's [20] are nonlinear in nature, showing maximum values at a specific w_{jk} 's accomplishing to extremely higher polarizations of polar molecules [16,21].

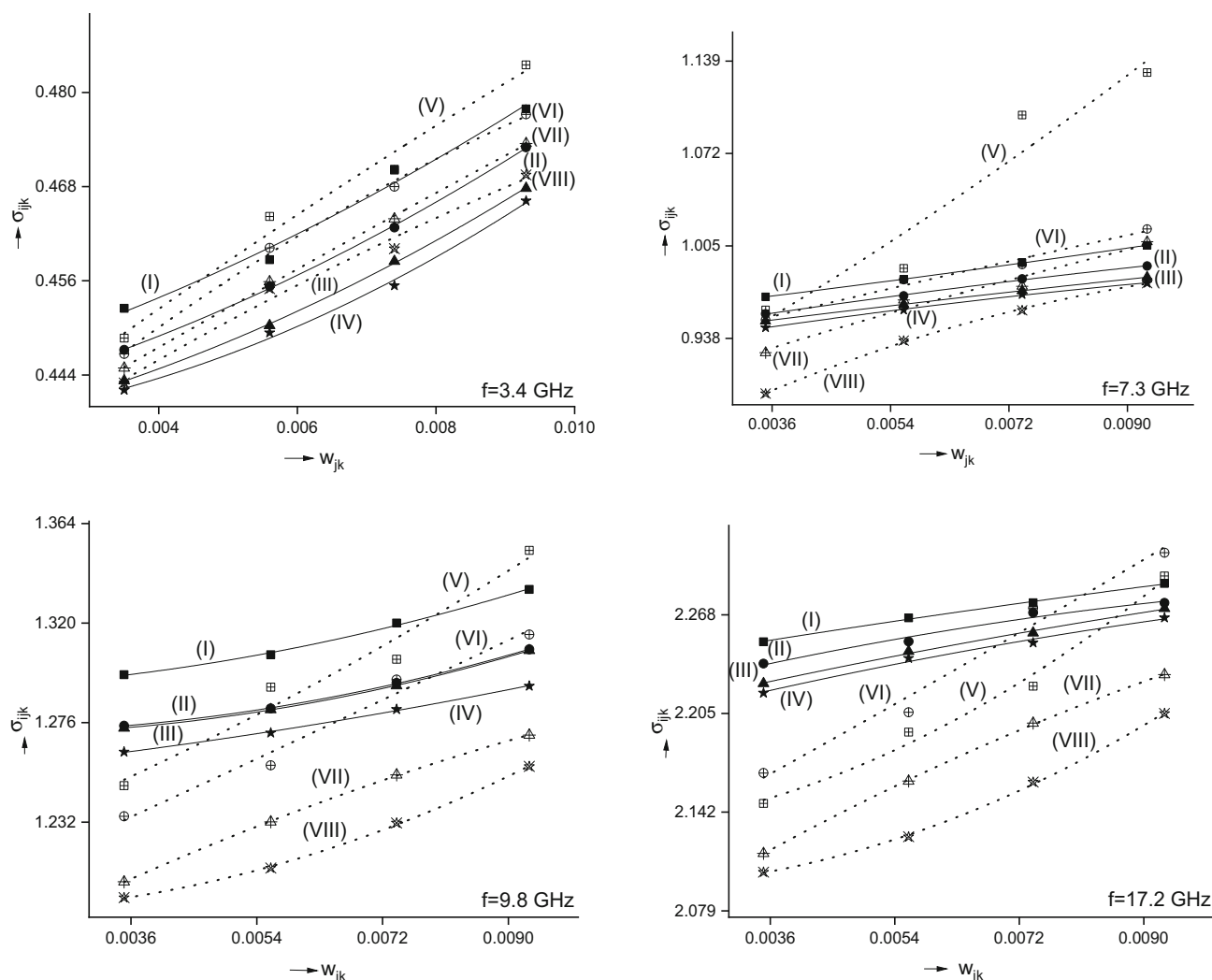


Figure 5. Variations of total conductivity σ_{ijk} against w_{jk} 's of DMF with pyridine or acetonitrile dissolved in p-xylene at different microwave field and temperatures. (I) \blacksquare at 25°C; (II) \bullet at 30°C; (III) \blacktriangle at 35°C; (IV) \star at 40°C for DMF + pyridine, respectively; (V) \boxplus at 25°C; (VI) \oplus at 30°C; (VII) \triangleleft at 35°C; (VIII) \times at 40°C for DMF + acetonitrile, respectively.

Each of the graphs are well fitted within the experimental values forming the usefulness of the proposed technique. σ_{ijk}'' vs. σ_{ijk}' graphs are noted linear in nature in figure 4, displaying the gradual increase of σ_{ijk}'' with σ_{ijk}' at different w_{jk} 's from 3.4 to 17.2 GHz. The graphs of σ_{ijk}'' vs. w_{jk} of figure 3 are almost same nature and magnitude with curves of total hf conductivity σ_{ijk} vs. w_{jk} of figure 5, indicating the utility of the assumption $\sigma_{ijk}'' \sim \sigma_{ijk}$ in the hf region [16]. The values of estimated τ 's of dual polar solution of DMF + pyridine or DMF + acetonitrile in p-xylene are decreasing with increase in temperature for a particular weight fraction of binary polar mixture. It proves that

Debye theory of dielectric relaxation principle [16] applicable to the polar–nonpolar mixtures under observation. It is also found that τ 's from equation (4) (ratio of slopes method) are lower than equation (5) of Murthy *et al* [18], as listed in table 2. The temperature dependence of τ 's shows higher τ 's at certain w_{jk} 's, as observed in figure 6, may be because of the solute–solute (dimer) molecular formation in the ternary solution that produces bigger size of molecular entity according to Debye relaxation mechanism [21]. τ 's from equation (4) are, however, very low for DMF + pyridine binary mixture at 35 and 40°C under 17.2 GHz. Such type of behaviour may be explained on the basis of solute–

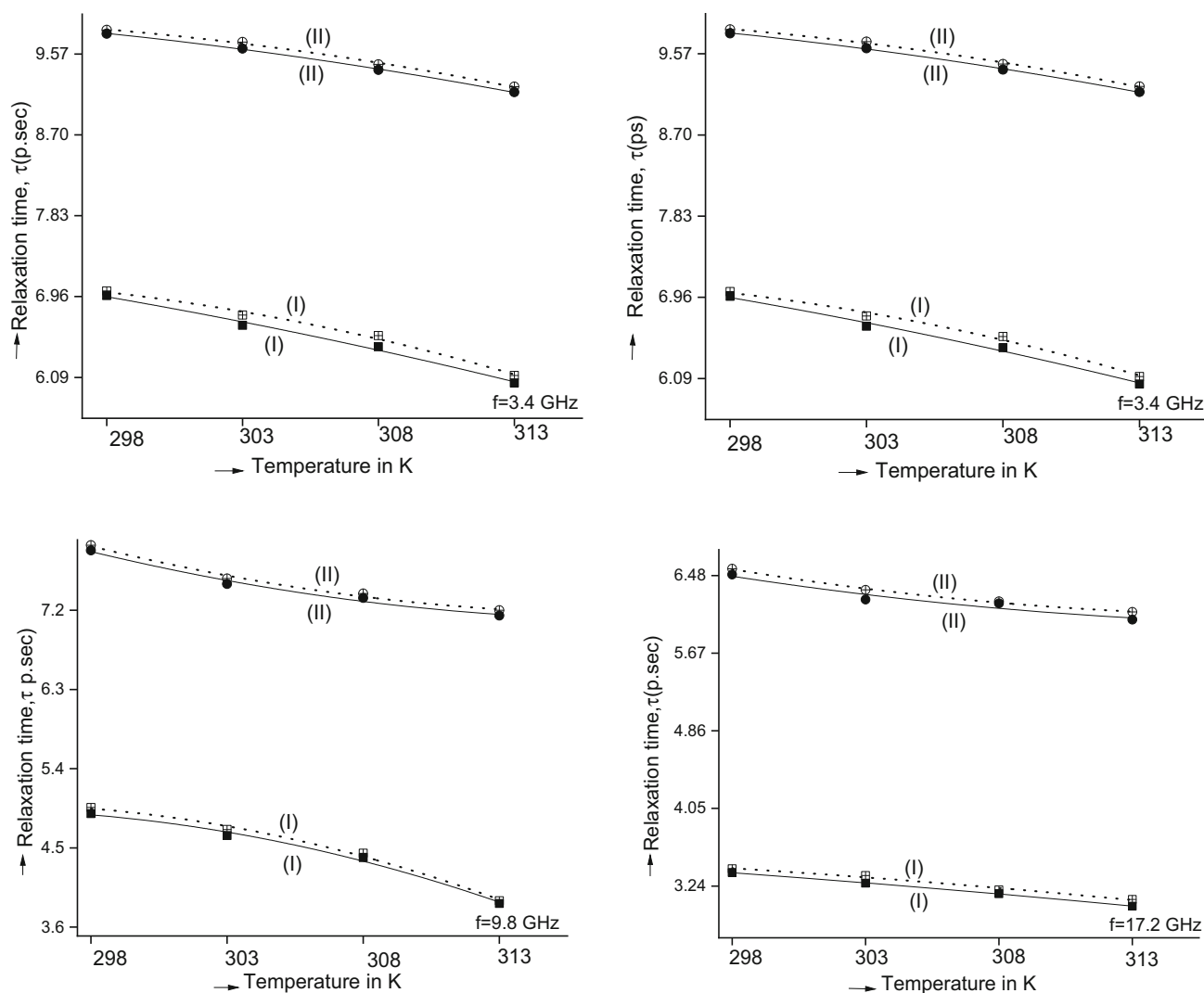


Figure 6. Variation of relaxation time τ_{jk} 's in ps against T in K of DMF with pyridine or acetonitrile dissolved in p-xylene under different microwave field from ratio of slope (—) and linear slope method (.....). (I) —■—; ...⊞... for DMF + pyridine, (II) —●—; ...⊕... for DMF + acetonitrile, respectively.

solvent (monomer) association for DMF + pyridine dissolved in p-xylene under microwave field at 35 and 40°C temperatures, respectively [20]. μ_{jk} 's are derived in terms of slope of σ_{ijk} vs. w_{jk} curve of figure 5 and listed in table 3. The graphs of μ 's are concave or convex in nature with change in temperature keeping w_{jk} as constant, as illustrated in figure 7. This kind of behaviour may be because of the stretching of bond moments and bond angles of the polar molecules with the increase of temperature in microwave region as observed before [21,22]. The thermodynamic energy constants [16] such as $\Delta H\tau$, $\Delta F\tau$ and $\Delta S\tau$ are derived from $\ln(\tau_{jk}T)$ vs. $1/T$ graphs and adopting slopes and intercepts of figure 8 for DMF(j) and pyridine(k) or

acetonitrile(k) and p-xylene(i) mixture assuming that polar-nonpolar mixture concurs Eyring rate theory [23]. The behaviour of $\ln(\tau_{jk}T)$ vs. $1/T$ for all the samples follow linear relationship signifying that dielectric relaxation process is a rate method [21]. The orderly nature of a structure under observation is perfectly estimated by entropy of a system ($\Delta S\tau$). $\Delta S\tau$'s are -ve for all the samples as listed in table 4, which indicate that the normal state is less well-arranged, as compared to activated states and cooperative in nature [17]. $\Delta H\tau$'s as well as ΔH_η exhibit +ve values for all systems, as shown in table 4. Enthalpy of activation is dependent on bonding pattern of the molecules and excitations to the activated states related to rupture of bonds.

Table 3. μ_{jk} from ratio of slopes of σ_{ijk}'' vs. w_{jk} and σ_{ijk}' vs. w_{jk} curve of equation (4), linear slope of σ_{ijk}'' vs. σ_{ijk}' curve of equation (5) of binary mixture of DMF and pyridine or acetonitrile dissolved in p-xylene at 25, 30, 35 and 40°C temperatures in various microwave field.

System	Frequency	Temperature	Measured $\mu_{jk} \times 10^{30}$ (C m ⁻¹) from σ_{ijk} measurement	
			Ratio of slopes of σ_{ijk}'' vs. w_{jk} and σ_{ijk}' vs. w_{jk} curve equations (4) and (6)	Linear slope of σ_{ijk}'' vs. σ_{ijk}' curve equations (5) and (6)
(I)DMF + pyridine	3.4	25	9.19	9.25
		30	9.23	9.31
		35	9.35	9.40
		40	9.46	9.65
	7.3	25	9.89	9.90
		30	10.11	10.23
		35	10.30	10.45
		40	10.42	10.66
	9.8	25	10.43	10.51
		30	10.72	10.80
		35	10.88	10.91
		40	11.05	11.19
	17.2	25	11.06	11.18
		30	11.38	11.56
		35	11.57	11.88
		40	11.76	12.10
(II)DMF + acetonitrile	3.4	25	11.21	11.33
		30	11.32	11.40
		35	11.54	11.61
		40	11.65	11.72
	7.3	25	11.47	11.54
		30	11.55	11.67
		35	11.76	11.83
		40	11.87	11.95
	9.8	25	12.07	12.15
		30	12.19	12.31
		35	12.31	12.40
		40	12.46	12.66
	17.2	25	12.21	12.33
		30	12.54	12.70
		35	12.76	12.85
		40	12.89	12.98

Dissimilarity in $\Delta H\tau$ and ΔH_{η} points out that relaxation procedure contains various types of creation and disruption of bonds to various range [17,21]. It is also observed that ΔF_{η} 's are greater than $\Delta F\tau$'s for both the systems, which indicate that dielectric relaxation mode follows rotation of the contributing molecules and the viscous mode accommodates both the translational and rotational movements [17]. The projected Debye factors ($\tau_{jk}T/\eta$) from all the proposed method are almost of same order. This proves that DMF + pyridine or DMF + acetonitrile with p-xylene

liquid mixture obey the Debye relaxation mechanism [14,18]. The solute–solute (dimer) relation occurred because of contact of fractional positive charge δ^+ on the edge of carbon atom of DMF and fractional negative charge δ^- on the edge of nitrogen atom of pyridine or acetonitrile, as illustrated in figure 9a and b. The solute–solvent (monomer) union is demonstrated in figure 9c and d, occurring because of contact of fractional negative charge δ^- on the edge of nitrogen atom of pyridine or acetonitrile with fractional positive charge δ^+

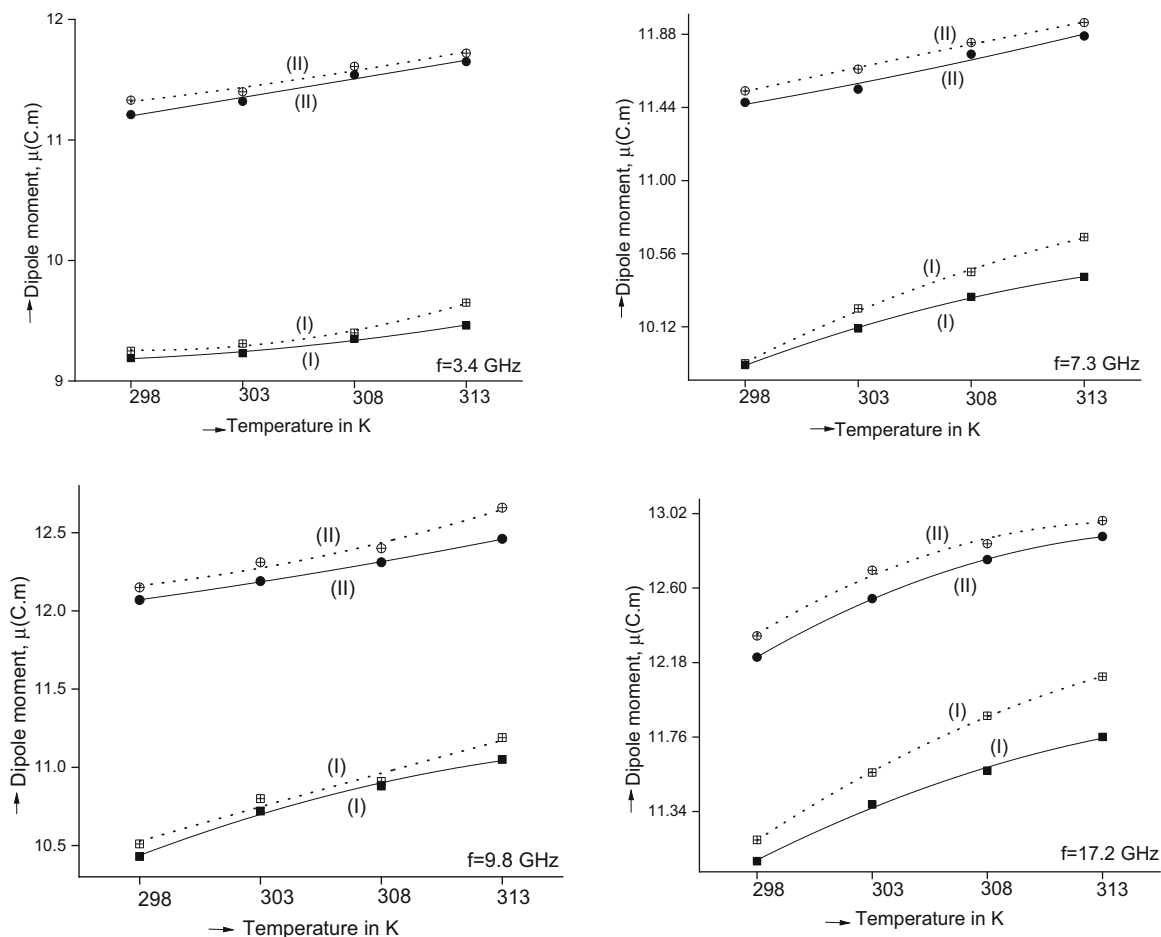


Figure 7. Variation of dipole moment μ_{jk} 's in C m^{-1} against T in K of DMF with pyridine or acetonitrile dissolved in p-xylene under different microwave field from ratio of slope (—) and linear slope method (.....). (I) —■—; ...■... for DMF + pyridine, (II) —●—; ...●... for DMF + acetonitrile, respectively.

at the edge of hydrogen atom of p-xylene, respectively. The dipole–dipole interaction follows in a manner that the resultant dipole moment gets amplified. Robust linear mutual dependence among dielectric parameter and w_{jk} 's indicates a possibility to fabricate a sensor based on dielectric spectral to identify concentration of binary polar mixture of DMF + pyridine or DMF + acetonitrile. The penetration depth should be strictly taken into account in advance of utilizing the dielectric property in detecting DMF, pyridine or acetonitrile quality in sample [17,19]. Overall, in the entire polar–nonpolar liquid mixture, the penetration depth decreases with rising frequency linearly, as illustrated in figure 10. It is observed that for a specific frequency, the penetration depth reduces with the rise in quantity of DMF + pyridine or DMF + acetonitrile mixture [17]. Under the indicated frequency spectrum (3.4 to 17.2 GHz), the penetration depths for DMF + pyridine or DMF + acetonitrile binary liquid mixture were greater than 20 mm. This distance should be adequate to perform dielectric experiment in the development of a sensor for the estimation of binary mixture concentration [17,19].

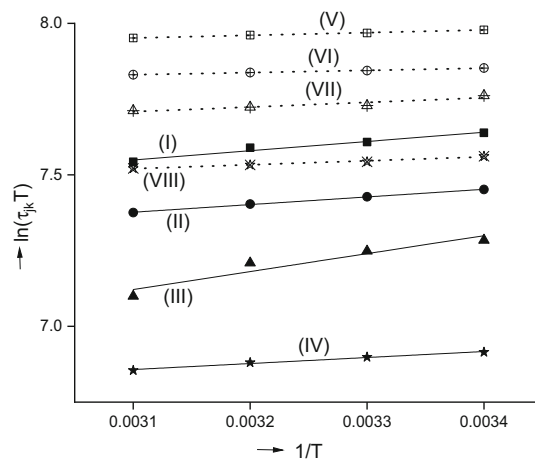


Figure 8. Variation of $\ln(\tau_{jk} T)$ against $1/T$ of DMF with pyridine or acetonitrile dissolved in p-xylene at different microwave field and temperatures. (I) —■— at 25°C; (II) —●— at 30°C; (III) —▲— at 35°C; (IV) —★— at 40°C for DMF + pyridine, respectively; (V) ...■... at 25°C; (VI) ...●... at 30°C; (VII) ...▲... at 35°C; (VIII) ...★... at 40°C for DMF + acetonitrile, respectively.

Table 4. Thermodynamic energy parameters such as enthalpy of activation $\Delta H\tau$, free energy of activation $\Delta F\tau$, entropy of activation $\Delta S\tau$ in the form $\ln(\tau_{jk}T)$ against $1/T$ curves using τ form conductivity measurement technique, Debye factor $\tau_{jk}T/\eta$, $\Delta F_{\eta} = (\Delta F\tau/\gamma)$, $\Delta H_{\eta} = (\Delta H\tau/\gamma)$ and $\Delta S_{\eta} = (\Delta S\tau/\gamma)$ for viscous flow process of DMF + pyridine or DMF + acetonitrile binary mixture dissolved in p-xylene at 25, 30, 35 and 40 °C temperatures in 3.4 GHz microwave field.

System	Temperature (°C)	$\Delta H\tau$ (kJ mol ⁻¹)	$\Delta F\tau$ (kJ mol ⁻¹)	$\Delta S\tau$ (kJ mol ⁻¹ K)	Debye factor ($\times 10^{-5}$)	$\Delta F_{\eta} = (\Delta F\tau/\gamma)$	$\Delta H_{\eta} = (\Delta H\tau/\gamma)$	$\Delta S_{\eta} = (\Delta S\tau/\gamma)$
(I)DMF + pyridine	25	1.35	1.99	-2.104	1.56	3.75	2.55	-3.970
	30		2.00	-2.098	1.70	3.77		-3.958
	35		2.01	-2.096	1.74	3.79		-3.955
	40		2.02	-2.095	1.82	3.81		-3.953
(II)DMF + acetonitrile	25	1.01	2.26	-4.16	2.19	6.11	2.73	-11.24
	30		2.29	-4.19	2.24	6.19		-11.32
	35		2.31	-4.21	2.42	6.24		-11.38
	40		2.34	-4.24	2.57	6.32		-11.46

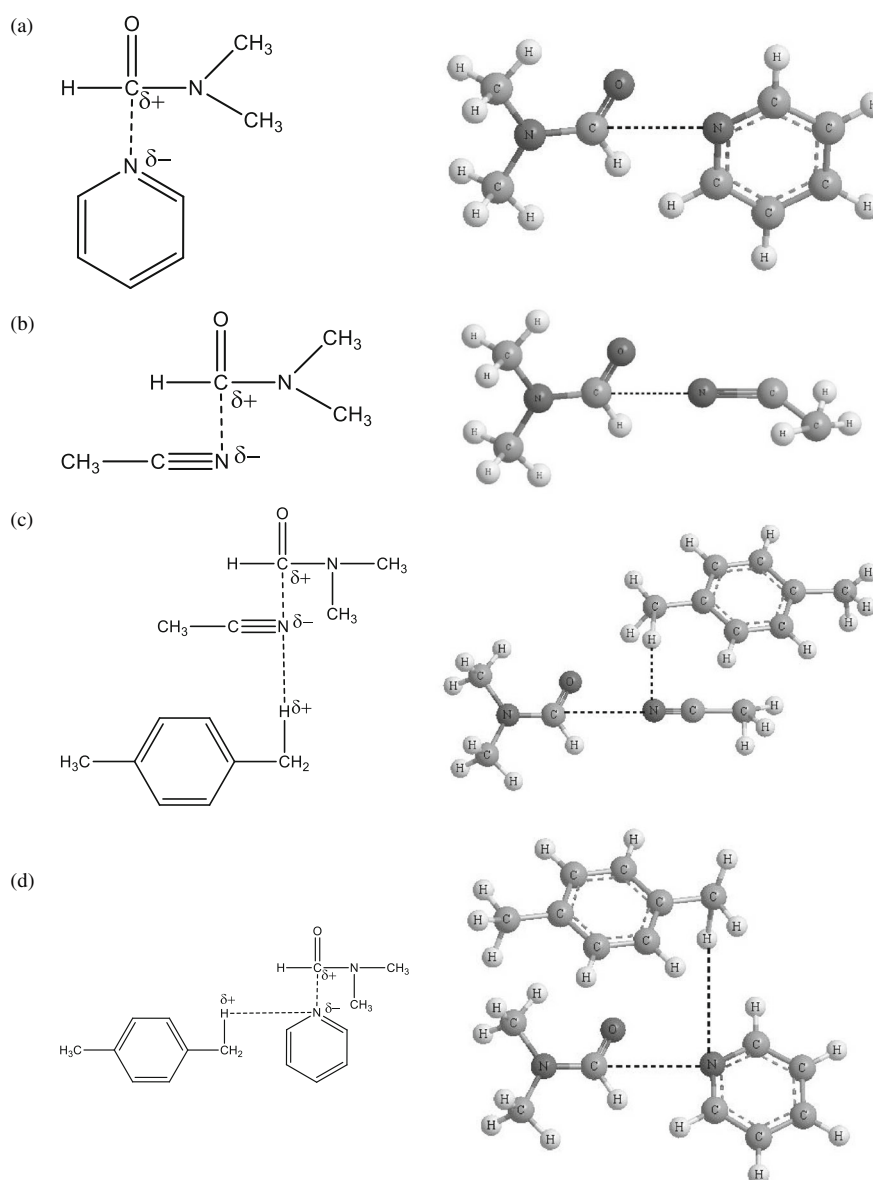


Figure 9. Various solute-solute and solute-solvent molecular association. (a) DMF + pyridine, (b) DMF + acetonitrile, (c) DMF + pyridine + p-xylene, (d) DMF + acetonitrile + p-xylene.

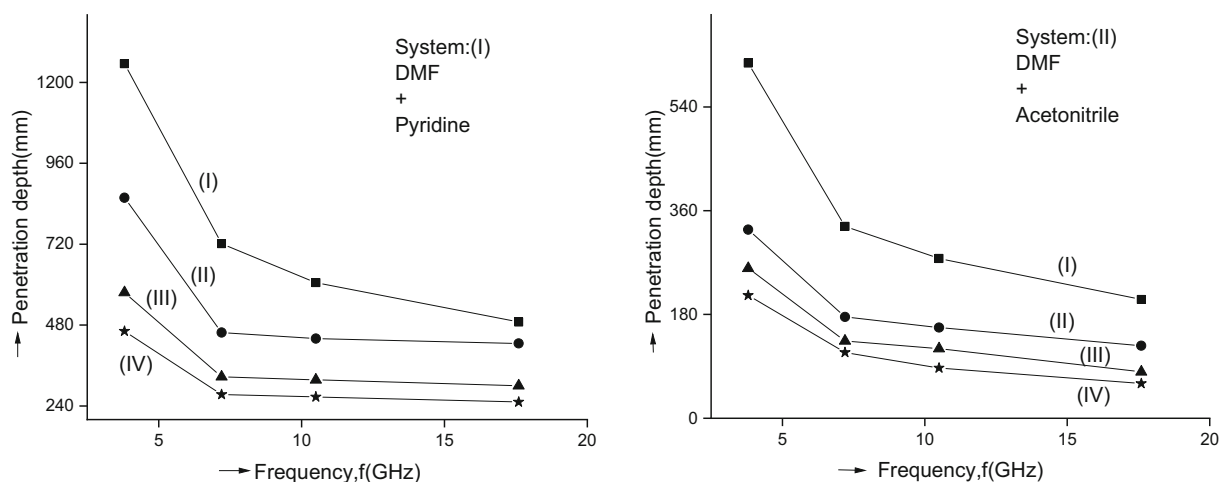


Figure 10. Concentration variation effect on penetration depth of DMF + pyridine and DMF + acetonitrile over the frequency range from 3.4 to 17.2 GHz at 25°C. (I) —■— for 0.0035; (II) —●— for 0.0056; (III) —▲— for 0.0074 and (IV) —★— for 0.0093 weight fraction of DMF + pyridine and DMF + acetonitrile, respectively.

5. Conclusion

Dielectric relaxation parameters τ and μ are analysed from conductivity (σ_{ijk}) data at different temperatures and microwave field using Debye model, analytically relating different physico-chemical characteristics of DMF, pyridine or acetonitrile. The variations of σ_{ijk}'' and σ_{ijk}' with w_{jk} at several frequencies either concave or convex demonstrate optimum data at particular w_{jk} . It reports the minimum or maximum polarization corresponding to intake of higher frequency electric field. Predicted τ 's decreases with increase in temperature following Debye relaxation mechanism. Different molecular formations are analysed from derived thermodynamic energy parameters or by the means of H-bonding and intercommunication of polar groups, as noticed from parabolic plot of τ_{jk} or μ_{jk} vs. temperature (T). In future, it is expected to develop sensor from appropriate penetration depth and dielectric constant of DMF, pyridine or acetonitrile.

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