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Dielectric relaxation of amides and tetrahydrofuran polar mixture in C_6H_6 from conductivity measurement under 9.90 GHz electric field

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Abstract. Dielectric relaxation studies of binary (jk) polar mixtures of tetrahydrofuran with N-methyl acetamide, N,N-dimethyl acetamide, N-methyl formamide and N,N-dimethyl formamide dissolved in benzene(i) for different weight fractions (w_{jk}'s) of the polar solutes and mole fractions (x_j's) of tetrahydrofuran at 25°C are attempted by measuring the conductivity of the solution under 9.90 GHz electric field using Debye theory. The estimated relaxation time (τ_{jk}'s) and dipole moment (μ_{jk}'s) agree well with the reported values signifying the validity of the proposed methods. Structural and associational aspects are predicted from the plot of τ_{jk} and μ_{jk} against x_j of tetrahydrofuran to arrive at solute–solute (dimer) molecular association upto $x_j = 0.3$ of tetrahydrofuran and thereafter solute–solvent (monomer) molecular association upto $x_j = 1.0$ for all systems except tetrahydrofuran + N,N-dimethyl acetamide.

1. Introduction

Dielectric relaxation of binary interacting solutes dissolved in nonpolar solvent provides meaningful information on the structural and associational aspects [1,2] as well as on the formation of molecular complexes under gigahertz (GHz) electric field and varying conditions of complexation, temperature and environmental factors [3,4]. The measured relaxation data are usually analysed within the framework of an appropriate model [5] of binary polar mixture to get parameters like relaxation time (τ_{jk}'s) and dipole moment (μ_{jk}'s) of the jk polar mixture. Tetrahydrofuran (THF) is an organic compound mainly used as a precursor to polymers. Being polar and having a wide liquid range, THF is a versatile industrial solvent for PVC and in varnishes. In the presence of strong acids, THF is converted into a linear polymer called polytetramethylene ether glycol (PTMEG), also known as polytetramethylene oxide (PTMO). This polymer is primarily used to make elastomeric polyurethane fibres like Spandex [6]. THF is a moderately polar solvent and can be used as an important

constituent of binary mixtures of required characteristics. The changes in τ and the distribution factor under the influence of THF as a solvent in dielectric relaxation process is insignificant. THF, being a class I liquid, has a common basis to the viscosity and polar relaxation exhibiting no rotational freedom in solid state. Amides like N-methyl acetamide (NMA), N,N-dimethyl acetamide (DMA) and N,N-dimethyl formamide (DMF) are non-aqueous aprotic solvents having wide applications and act as building blocks of proteins and enzymes. DMA is a good solvent of the polymer and the copolymer used in the spinning of artificial fibres. N-methyl formamide (NMF) is a specialized solvent in oil refineries. It is a precursor in specialized amidation reactions and used as a solvent in aluminum electrolytic capacitors.

Recently, Kumar *et al* [7–10] measured the dielectric relaxation parameters like real (ε'_{ijk}) and imaginary (ε''_{ijk}) parts of the complex relative permittivity (ε^*_{ijk}) of the binary (jk) or single j or k polar molecule of (THF+NMA), (THF+DMA), (THF+NMF), (THF+

DMF) dissolved in nonpolar solvent (i) benzene for different weight fractions w_{jk}'s, w_j's or w_k's at 25, 30, 35 and 40°C respectively for 0.0, 0.3, 0.5, 0.7 and 1.0 mole fractions (x_j's) of THF using standard standing wave microwave techniques and Gopalakrishna's single-frequency (9.90 GHz) concentration variational method [11]. They intended to predict the solute–solvent (monomer) types of molecular associations in the ternary mixture. The thermodynamic energy parameters for the dielectric relaxation and viscous flow process of the binary polar mixture were measured at different mole fractions of THF to arrive at the molecular environment.

We, therefore, thought to make an extensive study further with the available data on the binary (jk) polar mixture of (THF+NMA), (THF+DMA), (THF+NMF) and (THF+DMF) dissolved in C_6H_6 in terms of the measured real (σ'_{ijk}) and imaginary (σ''_{ijk}) parts of the high-frequency complex conductivity (σ^*_{ijk}) for different weight fractions (w_{jk}'s) of polar solutes at 9.90 GHz electric field under the identical state of molecular environment [7–10] in SI unit. The conductivity measurement technique is concerned with bound molecular charge of the polar molecules unlike permittivity (ε_{ijk}'s) and susceptibility (χ_{ijk}'s) which are related to all types of polarization and orientational polarization respectively. Recently, conductivity measurement technique [12] in the microwave electric fields has been successfully applied on binary polar mixture [13] as well as single polar liquid molecules [14] dissolved in nonpolar solvents. However, no such rigorous study has been made so far on the associative binary polar mixtures of (THF+NMA), (THF+DMA), (THF+NMF) and (THF+DMF) dissolved in C_6H_6 at a temperature under 9.90 GHz electric field using conductivity measurement technique. Dielectric measurement also has uses in package design, process control and physical chemical analysis [15]. The purpose of the conductivity measurement technique concerning bound molecular charge of the polar molecule allows one to link the results of dielectric studies to throw light on the structure and dynamics of polar liquid mixture in solution inferred from other techniques [11]. Under a definite temperature, dielectric relaxation phenomena should be closely related to variational frequency. After all, only the conductivity under 9.90 GHz is measured. Even though 9.90 GHz is the characteristic frequency of this dielectric relaxation, for different systems or the same system with different concentrations, the characteristic frequency of the dielectric relaxation may also be changed. The aim of the present paper is

also to see the applicability of conductivity measurement technique within the framework of Debye model in ternary liquid mixture under high-frequency (9.90 GHz) electric field like in the earlier paper [13].

2. Experimental procedure

The solvents THF, DMA, NMA, DMF and NMF are all good-quality samples. They were dried with occasional shaking and then distilled through a long vertical fractionating column [7–10]. The middle fraction of the sample was collected and mixed together for preparing the binary polar mixture of weight fractions w_{jk}'s dissolved in benzene. The X-band microwave was used to measure ε'_{ijk}, ε'_{ij}, ε'_{ik}, ε''_{ijk}, ε''_{ij}, ε''_{ik} at 25°C and different w_{jk}'s [7–10]. The temperature of the dielectric cell was maintained by circulating water and a thermostat. The measured ε'_{ijk} and ε''_{ijk} are accurate within ±0.5% and ±1.67% respectively.

3. Theoretical formulations

The σ^*_{ijk} due to the displacement current of a binary polar liquid mixture dissolved in nonpolar solvent(i) for a given w_{jk} of the solute is [16]

$$\sigma^*_{ijk} = \sigma'_{ijk} + j\sigma''_{ijk}, \tag{1}$$

where $\sigma'_{ijk} = \omega\varepsilon_0\varepsilon''_{ijk}$ and $\sigma''_{ijk} = \omega\varepsilon_0\varepsilon'_{ijk}$ are the real and imaginary parts of complex conductivity σ^*_{ijk} at different weight fractions (w_{jk}'s) of the polar mixture. ε_0 is the absolute permittivity of free space = 8.854×10^{-12} F·m^{-1}.

The total conductivity (σ_{ijk}) of the ternary solution is

$$\sigma_{ijk} = \omega\varepsilon_0\sqrt{(\varepsilon''^2_{ijk} + \varepsilon'^2_{ijk})} = \sqrt{(\sigma'^2_{ijk} + \sigma''^2_{ijk})}. \tag{2}$$

All the derived values of σ''_{ijk}, σ'_{ijk} and σ_{ijk} for different w_{jk}'s and mole fraction x_j's of THF are given in table 1.

The imaginary part of conductivity σ''_{ijk} is related to σ'_{ijk} by the following relation:

$$\sigma''_{ijk} = \sigma_{\infty ijk} + (1/\omega\tau_{jk})\sigma'_{ijk}$$

or

$$\tau_{jk} = 1/\omega\beta', \tag{3}$$

where β' is the slope of σ''_{ijk}–σ'_{ijk} linear relation as shown in figure 1 and given in table 2.

The constituent polar molecules mixed in appropriate proportions yield average τ_{jk} as:

$$\tau_{jk} = \tau_j x_j + \tau_k x_k, \tag{4}$$

Table 1. Measured dielectric relaxation parameters such as real σ'_{ijk} $(=\omega\varepsilon_0\varepsilon''_{ijk})$ and imaginary σ''_{ijk} $(=\omega\varepsilon_0\varepsilon'_{ijk})$ parts of total high frequency conductivity σ_{ijk} $(=\sqrt{(\sigma'_{ijk})^2+(\sigma''_{ijk})^2})$ for different weight fractions w_{jk}'s of the binary polar mixtures THF+NMA, THF+DMA, THF+NMF and THF+DMF dissolved in C_6H_6 at 25°C under 9.90 GHz electric field.

System	Mole fraction of THF in binary mixture	Weight fraction	σ'_{ijk} $(\Omega^{-1}m^{-1})$	σ''_{ijk} $(\Omega^{-1}m^{-1})$	σ_{ijk} $(\Omega^{-1}m^{-1})$
I(a) THF+NMA in C_6H_6	0.00	0.00182	0.0086	1.2667	1.2667
		0.00302	0.0118	1.2739	1.274
		0.00412	0.0146	1.2794	1.2795
		0.00508	0.02	1.2893	1.2895
		0.00654	0.0229	1.2987	1.2989
I(b) THF+NMA in C_6H_6	0.30	0.00288	0.0086	1.2695	1.2695
		0.00430	0.0123	1.2794	1.2795
		0.00584	0.0178	1.2871	1.2872
		0.00667	0.0208	1.2932	1.2934
		0.00752	0.0242	1.2959	1.2961
I(c) THF+NMA in C_6H_6	0.50	0.00236	0.0063	1.2629	1.2629
		0.00387	0.0084	1.2667	1.2667
		0.00541	0.0107	1.2722	1.2722
		0.00718	0.0139	1.2794	1.2795
		0.00945	0.0178	1.2871	1.2872
I(d) THF+NMA in C_6H_6	0.70	0.00386	0.0069	1.2508	1.2508
		0.00518	0.009	1.2579	1.2579
		0.00720	0.0112	1.2656	1.2656
		0.00815	0.0124	1.2684	1.2685
		0.00953	0.0151	1.2739	1.274
I(e) THF+NMA in C_6H_6	1.00	0.00531	0.0029	1.248	1.248
		0.00873	0.0036	1.2574	1.2574
		0.0120	0.0044	1.2684	1.2684
		0.0196	0.0074	1.2893	1.2893
		0.0266	0.0081	1.3075	1.3075
II(a) THF+DMA in C_6H_6	0.00	0.00249	0.0073	1.27	1.2700
		0.00385	0.0104	1.2816	1.2816
		0.00471	0.0128	1.2893	1.2894
		0.00574	0.0153	1.297	1.2971
		0.00681	0.0185	1.3069	1.307
II(b) THF+DMA in C_6H_6	0.30	0.00243	0.0058	1.2629	1.2629
		0.00326	0.0068	1.2673	1.2673
		0.00476	0.0093	1.2761	1.2761
		0.00559	0.01	1.2794	1.2794
		0.00739	0.0133	1.291	1.2911
II(c) THF+DMA in C_6H_6	0.50	0.00325	0.0054	1.2629	1.2629
		0.00493	0.008	1.275	1.2750
		0.00571	0.0093	1.2832	1.2832
		0.00721	0.0112	1.2948	1.2948
		0.00856	0.0133	1.3047	1.3048
II(d) THF+DMA in C_6H_6	0.70	0.0033	0.0055	1.2629	1.2629
		0.00496	0.007	1.2739	1.2739
		0.0067	0.0085	1.2855	1.2855
		0.00841	0.01	1.2987	1.2987
		0.0105	0.0121	1.3124	1.3125

Table 1. *Continued.*

System	Mole fraction of THF in binary mixture	Weight fraction	σ'_{ijk} $(\Omega^{-1}\text{m}^{-1})$	σ''_{ijk} $(\Omega^{-1}\text{m}^{-1})$	σ_{ijk} $(\Omega^{-1}\text{m}^{-1})$
II(e) THF+DMA in C_6H_6	1.00	0.00531	0.0029	1.248	1.248
		0.00873	0.0036	1.2574	1.2574
		0.012	0.0044	1.2684	1.2684
		0.0196	0.0074	1.2893	1.2893
		0.0266	0.0081	1.3075	1.3075
III(a) THF+NMF in C_6H_6	0.00	0.00204	0.0074	1.2799	1.2799
		0.00343	0.0128	1.2948	1.2949
		0.0043	0.0166	1.3086	1.3087
		0.00511	0.0206	1.3185	1.3187
		0.00639	0.0262	1.335	1.3353
III(b) THF+NMF in C_6H_6	0.30	0.00249	0.0066	1.2645	1.2645
		0.00341	0.0087	1.27	1.27
		0.00539	0.0149	1.2855	1.2856
		0.00643	0.0175	1.2921	1.2922
		0.00757	0.0213	1.3003	1.3005
III(c) THF+NMF in C_6H_6	0.50	0.00374	0.0076	1.2535	1.2535
		0.00518	0.0096	1.259	1.259
		0.00699	0.0137	1.2722	1.2723
		0.00858	0.0166	1.2816	1.2817
		0.011	0.0207	1.2932	1.2934
III(d) THF+NMF in C_6H_6	0.70	0.00291	0.0052	1.2519	1.2519
		0.0052	0.0074	1.2645	1.2645
		0.00684	0.0093	1.2739	1.2739
		0.00837	0.0107	1.2832	1.2832
		0.0126	0.015	1.3047	1.3048
III(e) THF+NMF in C_6H_6	1.00	0.00531	0.0029	1.248	1.248
		0.00873	0.0036	1.2574	1.2574
		0.012	0.0044	1.2684	1.2684
		0.0196	0.0074	1.2893	1.2893
		0.0266	0.0081	1.3075	1.3075
IV(a) THF+DMF in C_6H_6	0.00	0.00311	0.0101	1.2667	1.2667
		0.0041	0.0124	1.2761	1.2762
		0.00537	0.0162	1.2893	1.2894
		0.00625	0.0191	1.3009	1.301
		0.0073	0.0218	1.3086	1.3088
IV(b) THF+DMF in C_6H_6	0.30	0.00272	0.0093	1.2645	1.2645
		0.0037	0.0111	1.2722	1.2722
		0.00481	0.0131	1.2794	1.2795
		0.00635	0.0155	1.2888	1.2889
		0.0076	0.0188	1.2987	1.2988
IV(c) THF+DMF in C_6H_6	0.50	0.00285	0.008	1.2684	1.2684
		0.00459	0.0107	1.275	1.275
		0.00618	0.012	1.2783	1.2784
		0.00758	0.014	1.2832	1.2833
		0.0117	0.0197	1.297	1.2971
IV(d) THF+DMF in C_6H_6	0.70	0.00336	0.0055	1.2684	1.2684
		0.00703	0.008	1.2794	1.2794
		0.0124	0.0137	1.2987	1.2988
		0.0151	0.0174	1.3124	1.3125
		0.0197	0.0217	1.3284	1.3286

Table 1. *Continued.*

System	Mole fraction of THF in binary mixture	Weight fraction	σ'_{ijk} ($\Omega^{-1}m^{-1}$)	σ''_{ijk} ($\Omega^{-1}m^{-1}$)	σ_{ijk} ($\Omega^{-1}m^{-1}$)
IV(e) THF+DMF in C_6H_6	1.00	0.00531	0.0029	1.248	1.248
		0.00873	0.0036	1.2574	1.2574
		0.012	0.0044	1.2684	1.2684
		0.0196	0.0074	1.2893	1.2893
		0.0266	0.0081	1.3075	1.3075

Figure 1. Linear variation of the imaginary part of conductivity (σ''_{ijk}) against real part of conductivity (σ'_{ijk}) in $\Omega^{-1}m^{-1}$ of the binary polar mixture (**a**) NMA+THF, (**b**) DMA+THF, (**c**) NMF+THF and (**d**) DMF+THF dissolved in C_6H_6 at 25°C under 9.90 GHz electric field for 0.0 (—■—), 0.3 (—●—), 0.5 (—▲—), 0.7 (—★—) and 1.0 (—●—) x_j of THF respectively.

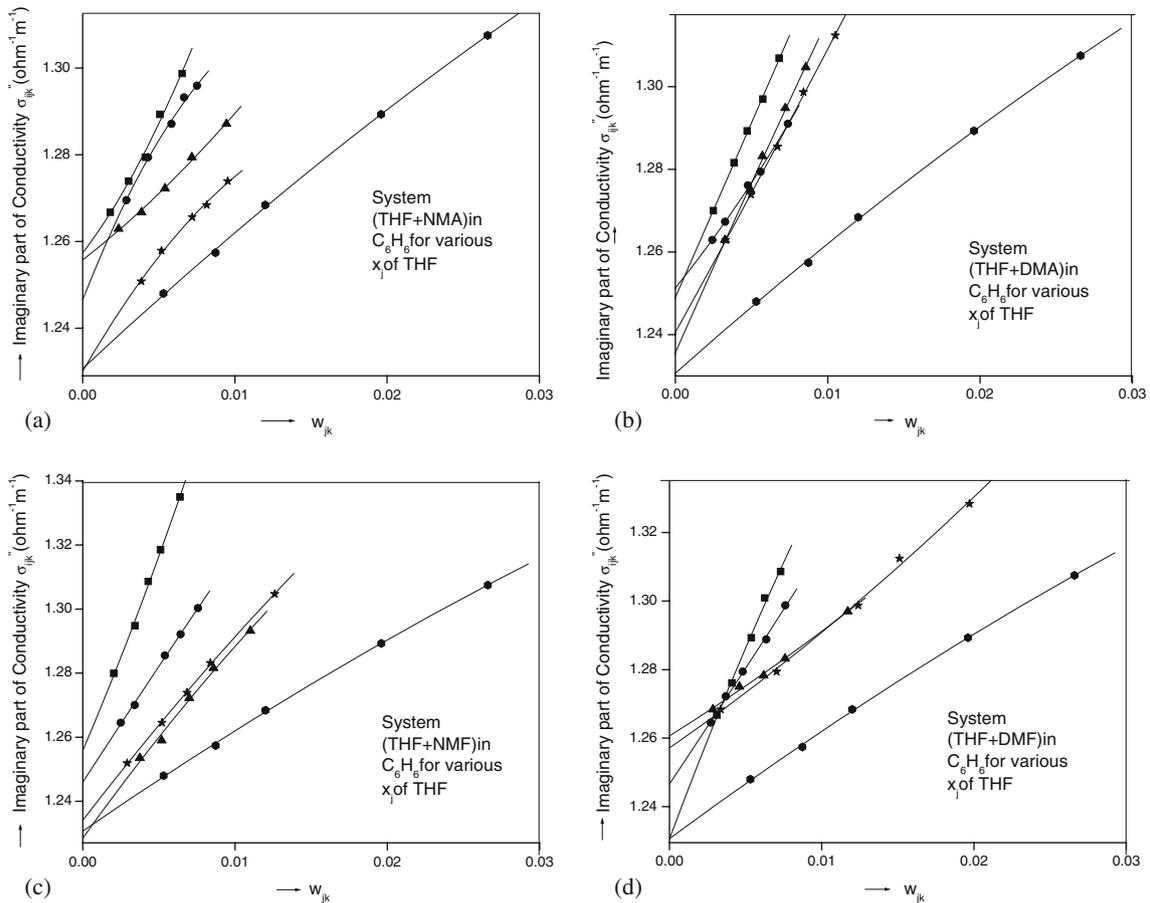where x_j and x_k are the mole fractions of THF (j) and amide (k).

Both σ''_{ijk} and σ'_{ijk} are functions of w_{jk}'s at different temperatures. To eliminate the effect of polar–polar interactions in the estimation of τ_{jk}, one can safely use eq. (3) in the following form:

$$\tau_{jk} = \frac{1}{\omega}\frac{\beta_2}{\beta_1}, \tag{5}$$

Table 2. Measured relaxation times τ's using σ''_{ijk}–σ'_{ijk} linear curve (eq. (3)) as well as the ratio of slopes of σ''_{ijk}–w_{jk} and σ'_{ijk}–w_{jk} curves when $w_{jk} \to 0$ of eq. (5), reported τ's due to Gopalakrishna method, average τ_{jk} from eqs (3) and (5) of the binary polar mixtures THF+NMA, THF+DMA, THF+NMF and THF+DMF dissolved in C_6H_6 at 25°C for different mole fractions 0.0, 0.3, 0.5, 0.7 and 1.0 of THF under 9.90 GHz electric field.

System	Mole fraction of THF in binary mixture	Slope of σ''_{ijk}–σ'_{ijk} curves of eq. (3)	Ratio of slopes of σ''_{ijk}–w_{jk} and σ'_{ijk}–w_{jk} curves when $w_{jk} \to 0$ eq. (5)	τ's in ps from eq. (3)	τ's in ps from eq. (5)	Reported τ's in ps (Gopalakrishna method)	Calculated average τ_{jk} $= \tau_j x_j + \tau_k x_k$ in ps from eq. (4)	Coefficients of τ_{jk}–x_j curves		
(I) THF +NMA in C_6H_6	(a) 0.00	2.14804	1.4918	7.48	10.78	6.26	10.78	1.00321×10^{-11}	-1.70053×10^{-11}	9.07255×10^{-12}
	(b) 0.30	1.68224	6.0726	9.56	2.68	7.27	8.14			
	(c) 0.50	2.14180	2.2480	7.51	7.15	6.02	6.39	$(7.78694 \times 10^{-12}$	6.89373×10^{-12}	$-1.33437 \times 10^{-11})$
	(d) 0.70	2.85738	9.7587	5.63	1.65	5.38	4.63			
	(e) 1.00	10.2083	8.0811	1.57	1.99	1.29	1.99			
(II) THF +NMF in C_6H_6	(a) 0.00	3.26904	4.6469	4.92	3.46	4.18	3.46	3.64015×10^{-12}	-8.53951×10^{-13}	-1.03053×10^{-12}
	(b) 0.30	3.72625	4.4163	4.31	3.64	3.78	3.02			
	(c) 0.50	5.41651	4.9671	2.97	3.24	2.64	2.73	$(5.08178 \times 10^{-12}$	-4.27089×10^{-12}	$6.32961 \times 10^{-13})$
	(d) 0.70	7.62210	8.6675	2.11	1.85	1.92	2.43			
	(e) 1.00	10.2083	8.0811	1.58	1.99	1.29	1.99			
(III) THF +DMA in C_6H_6	(a) 0.00	2.94574	3.1899	5.46	5.04	4.85	5.04	5.22463×10^{-12}	3.04412×10^{-13}	-3.81648×10^{-12}
	(b) 0.30	2.45416	3.0561	6.55	5.26	5.57	4.13			
	(c) 0.50	3.07292	3.2775	5.23	4.91	4.58	3.52	$(5.6947 \times 10^{-12}$	3.89989×10^{-12}	$-9.83782 \times 10^{-12})$
	(d) 0.70	5.39515	5.9642	2.98	2.70	2.58	2.91			
	(e) 1.00	10.2083	8.0811	1.57	1.99	1.29	1.99			
(IV) THF +DMF in C_6H_6	(a) 0.00	3.60733	4.9174	4.46	3.27	3.70	3.27	2.71832×10^{-12}	8.37426×10^{-12}	-8.86737×10^{-12}
	(b) 0.30	3.60501	6.5252	4.46	2.46	4.16	2.89			
	(c) 0.50	2.44499	2.5321	6.58	6.35	5.80	2.63	$(4.16732 \times 10^{-12}$	7.80671×10^{-12}	$-1.03188 \times 10^{-11})$
	(d) 0.70	3.64990	3.7975	4.40	4.23	3.86	2.37			
	(e) 1.00	10.2083	8.0811	1.57	1.99	1.29	1.99			

Figure 2. The variation of the imaginary part of conductivity (σ''_{ijk}) ($\Omega^{-1}m^{-1}$) against weight fractions (w_{jk}'s) of the binary polar mixture (**a**) NMA+THF, (**b**) DMA+THF, (**c**) NMF+THF and (**d**) DMF+THF dissolved in C_6H_6 at 25°C under 9.90 GHz electric field for 0.0 (—■—), 0.3 (— • —), 0.5 (—▲—), 0.7 (—★—) and 1.0 (—●—) x_j of THF respectively.

where β_1 and β_2 are respectively the slopes of $\sigma''_{ijk}–w_{jk}$ and $\sigma'_{ijk}–w_{jk}$ curves when $w_{jk} \to 0$ (see figures 2 and 3 and table 2). τ's are estimated from both eqs (3) and (5) and they are placed in table 2 for different x_j's of THF along with the reported τ's due to Gopalakrishna method [11].

In the high-frequency region, $\sigma''_{ijk} \approx \sigma_{ijk}$ eq. (3) can now be written as

$$\beta = \frac{1}{\omega\tau_{jk}}\left(\frac{\mathrm{d}\sigma'_{ijk}}{\mathrm{d}w_{jk}}\right)_{w_{jk}\to 0}, \tag{6}$$

where β is the slope of $\sigma_{ijk}–w_{jk}$ curves of figure 4 when $w_{jk} \to 0$ and the values are given in table 3. The estimated τ_{jk} and μ_{jk} of tables 2 and 3 are plotted against x_j of the THF as seen in figures 5 and 6.

When $w_{jk} \to 0$, the real part σ'_{ijk} of a binary polar–nonpolar liquid mixture of w_{jk} at T K is given by [13,17]

$$\left(\frac{\mathrm{d}\sigma'_{ijk}}{\mathrm{d}w_{jk}}\right)_{w_{jk}\to 0} = \frac{N\rho_i\mu_{jk}^2}{3M_{jk}K_BT}\frac{\omega^2\tau_{jk}}{(1+\omega^2\tau_{jk}^2)_x} \\ \times \frac{(\varepsilon_i+2)^2}{3^2}, \tag{7}$$

where μ_{jk} is the dipole moment of the binary polar mixture of molecular weight $M_{jk} = M_jx_j + M_kx_k$; x_j being the mole fractions of THF in the binary polar mixture of j(THF) and k(amide) such that $x_j + x_k = 1$. The other terminologies and symbols are of usual significance [5]. On comparison of eqs (6) and (7) one gets

$$\mu_{jk} = \left[\frac{27M_{jk}K_BT\beta}{N\rho_i(\varepsilon_i+2)^2\,\omega b}\right]^{1/2}, \tag{8}$$
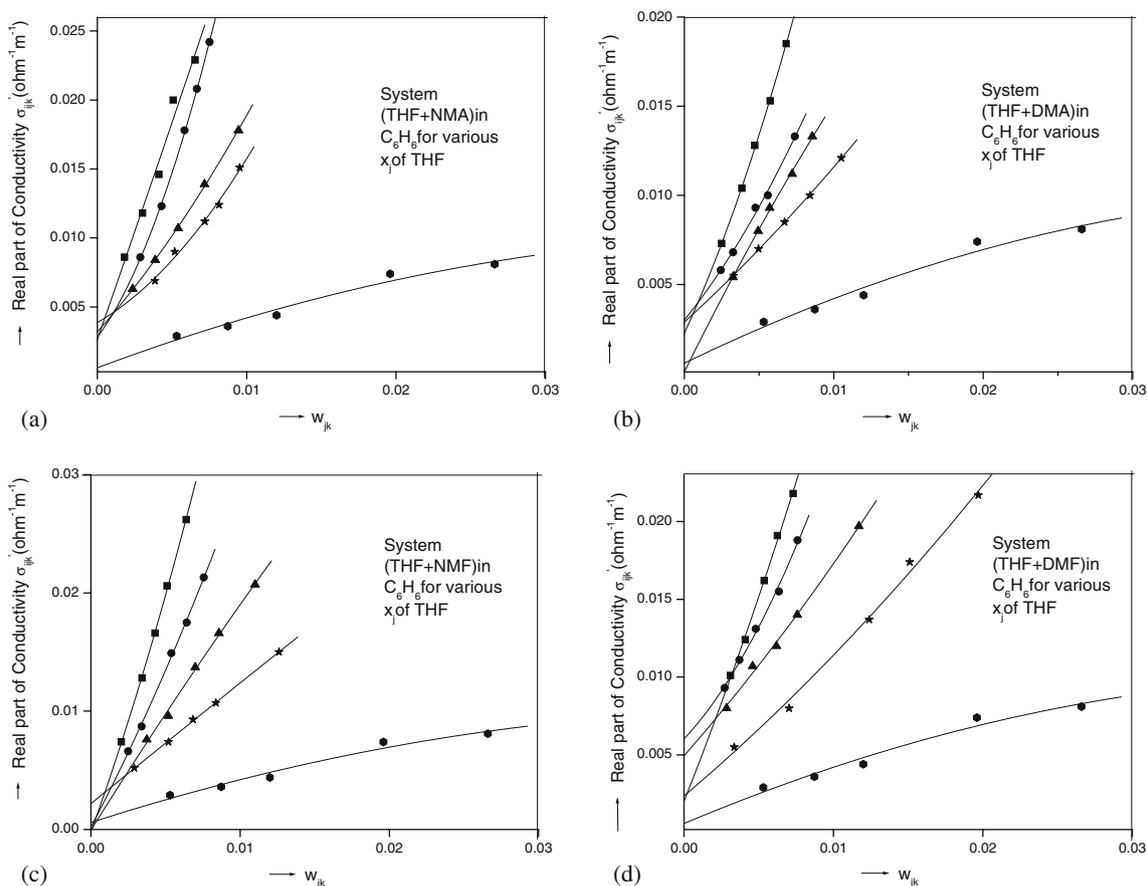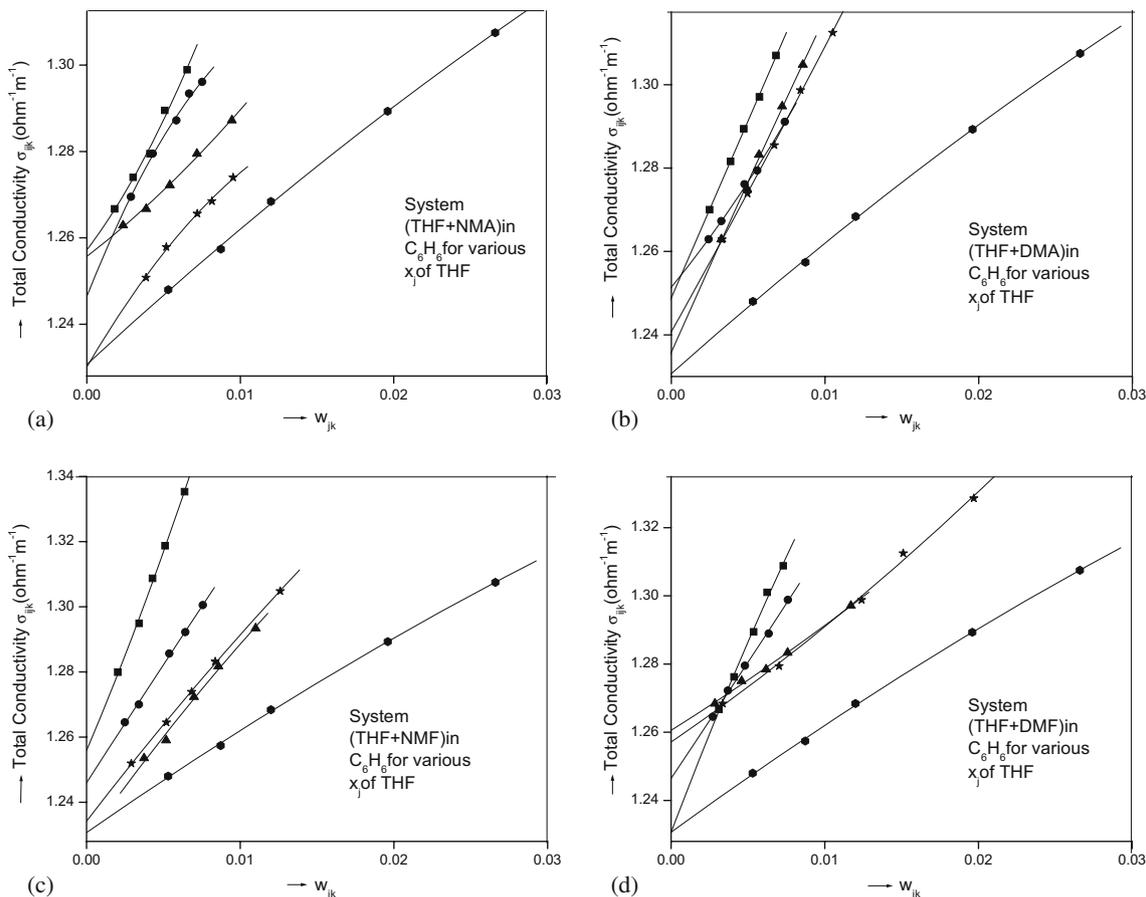
Figure 3. The variation of the real part of conductivity (σ'_{ijk}) ($\Omega^{-1}\text{m}^{-1}$) against weight fractions (w_{jk}'s) of the binary polar mixture (**a**) NMA+THF, (**b**) DMA+THF, (**c**) NMF+THF and (**d**) DMF+THF dissolved in C_6H_6 at 25°C under 9.90 GHz electric field for 0.0 (—■—), 0.3 (—●—), 0.5 (—▲—), 0.7 (—★—) and 1.0 (—●—) x_j of THF respectively.

where $b = 1/(1 + \omega^2\tau_{jk}^2)$ is the dimensionless parameter. The other symbols used in eq. (8) carry usual meanings [5] in SI unit. All the μ's at different x_j's of THF along with μ_{theo}'s of figure 6 are shown in table 3.

4. Results and discussions

The normalized conductivity data σ_{ijk}'s [16] of binary (jk) polar mixture of THF(j) with kth polar components like NMA, DMA, NMF and DMF dissolved in benzene(i) for different weight fractions w_{jk}'s and mole fractions x_j's of THF at 25°C are presented in table 1. They are utilized to estimate τ_{jk} of the binary polar mixture from the slope of the linear relation σ''_{ijk} against σ'_{ijk} curves of figure 1. Figure 1 reveals that the curves are perfectly linear as evident from the values of correlation coefficient r; $-1 \leq r \leq 1$. Slopes of pure THF in all the four binary polar mixtures are high and almost constant as evident from table 2 to yield low τ ($\sim$1.58 ps). This is probably due to the

rigid nature of THF molecule which exists in monomer form. The gradual increase of slope with the increase of x_j of THF is observed for THF+DMA(II) and THF+NMF(III) in figure 1 which in turn gives low τ according to table 2. Similar trend along with almost the same slope is observed at $x_j = 0.0$, 0.3 and 0.5 of THF for THF+NMA(I) and THF+DMF(IV) binary polar mixture indicating perhaps the same polarity of the constituent polar molecules [18]. τ's were also estimated using the ratio of slopes of σ''_{ijk}–w_{jk} and σ'_{ijk}–w_{jk} curves of figures 2 and 3 when $w_{jk} \to 0$. From figures 2 and 3, we can observe that values of σ''_{ijk} and σ'_{ijk}, being functions of w_{jk}, increase gradually with w_{jk} to exhibit high values for pure amides (i.e., $x_j = 0.0$) and then decrease chronologically upto $x_j = 1.0$ of THF. This type of behaviour reveals that the polar molecules exhibit maximum polarization for high absorption of high-frequency electric energy as observed earlier [16]. The polarization, however, is the same for systems THF+DMA(II) and THF+DMF(IV) for $0.0 \leq w_{jk} \leq 0.01$ at $x_j = 0.0$–0.7 of THF indicating
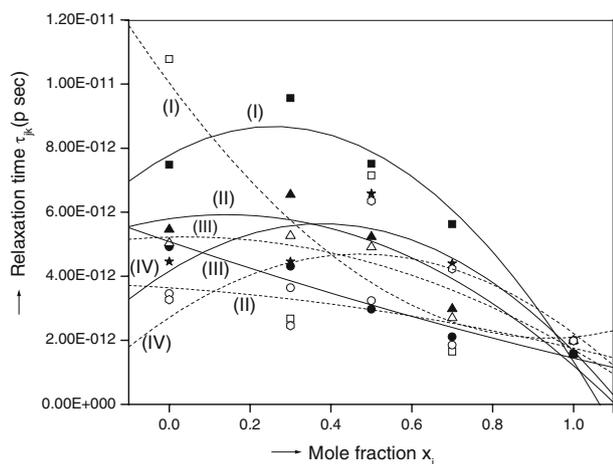
Figure 4. The variation of total conductivity (σ_{ijk}) ($\Omega^{-1}\text{m}^{-1}$) against weight fractions (w_{jk}'s) of the binary polar mixture (**a**) NMA+THF, (**b**) DMA+THF, (**c**) NMF+THF and (**d**) DMF+THF dissolved in C_6H_6 at 25°C under 9.90 GHz electric field for 0.0 (—■—), 0.3 (—●—), 0.5 (—▲—), 0.7 (—★—) and 1.0 (—●—) x_j of THF respectively.

the same polarity as observed in σ_{ijk}''–σ_{ijk}' curves of figure 1. The σ_{ijk}–w_{jk} curves in figure 4 are parabolic and identical in nature to σ_{ijk}''–w_{jk} curves of figure 2 signifying the validity of $\sigma_{ijk}'' \approx \sigma_{ijk}$ in eq. (3). As evident from figure 5 and table 2, unlike DMA(II) τ_{jk}–x_j curves from both the proposed methods increase nonlinearly from $x_j = 0.0$ to 0.3 and 0.5 for NMA(I), NMF(III) and DMF(IV) respectively to attain maximum value and then decreases gradually to yield almost constant value at $x_j = 1.0$ of THF. This type of behaviour indicates that solute–solute (dimer) [19] molecular association upto $x_j = 0.3$ or 0.5 and solute–solvent (monomer) molecular association happens thereafter upto $x_j = 1.0$ THF except THF+DMA(II) as observed in [7–10]. A fraction of associative pairs of THF+amides will break as THF and amide alone under high-frequency electric field to yield smaller μ for the monomer. The dipole moments μ's of the polar mixtures are estimated using τ from figures 3 and 5 and slope β of σ_{ijk}–w_{jk} curves of figure 4. They are given in table 3 along with the

reported μ's due to Gopalakrishna method and μ's from simple mixing rule. Unlike THF+DMF(IV) in figure 6, the variation of μ_{jk} against x_j's are parabolic showing higher μ's around $x_j = 0.3$ and then decreases gradually to attain a minimum value at $x_j = 1.0$ of THF. This type of behaviour signifies the existence of solute–solute (dimer) and solute–solvent (monomer) molecular association upto $x_j = 0.3$ and thereafter as observed in the case of τ_{jk}–x_j curve of figure 5. The chemical structure of the polar molecules are sketched in figure 7 from the fixed bond moments [12] of 1×10^{-30}, 3.33×10^{-30}, 1.5×10^{-30}, 2.13×10^{-30}, 4.33×10^{-30}, 1.23×10^{-30} and 10.33×10^{-30} C·m of C↘H, C↘O, N↘C, CH_3↘N, H↘N, C↘CH_3 and O⇄C substituent polar groups aligned at an angle to the chain. The vectorial addition of bond moments assuming the planar structure of the molecules leads to theoretical dipole moments (μ_{theo}'s) as given in table 3. There also exist inductive, mesomeric and electromeric effects within the substituent polar groups causing difference in electron affinity in them. The solute–solute

Table 3. Slopes β's of $\sigma_{ijk}-w_{jk}$ curve, dimensionless parameters b's in terms of τ's from eqs (3) and (5), measured μ's in two methods, average $\mu_{jk} = \mu_j x_j + \mu_k x_k$, reported μ's as well as μ_{theo}'s in C·m of THF + NMA, THF + DMA, THF + NMF and THF + DMF binary polar mixtures dissolved in C_6H_6 for 0.0, 0.3, 0.5, 0.7 and 1.0 mole fractions of THF at 25°C under 9.90 GHz electric field.

| System	Mole fraction of THF in binary mixture	Slope β's of $\sigma_{ijk}-w_{jk}$ curve of eq. (6)	$b = \frac{1}{1+\omega^2\tau^2}$ from τ of eq. (3)	$b = \frac{1}{1+\omega^2\tau^2}$ from τ of eq. (5)	$\mu_{jk} \times 10^{-30}$ C·m from eqs (3) and (8)	$\mu_{jk} \times 10^{-30}$ C·m from eqs (5) and (8)	Reported $\mu_{jk} \times 10^{-30}$ C·m	Average $\mu_{jk} \times 10^{-30}$ C·m $\mu_{jk} = \mu_j x_j + \mu_k x_k$	Theoretical $\mu_{\text{theo}} \times 10^{-30}$ C·m
(I) THF + NMA in C_6H_6	(a) 0.00	4.69545	1.3118	1.0095	8.80	9.61	3.33	9.61	15.44 [16]
	(b) 0.30	8.86139	1.2165	1.4496	12.73	11.09		8.73	12.43
	(c) 0.50	2.74334	1.3536	1.0278	6.71	6.65		8.14	
	(d) 0.70	6.02531	1.2182	1.1978	9.53	9.04	1.85	7.55	5.78
	(e) 1.00	3.27495	1.1226	1.0105	6.64	6.67		6.67	
(II) THF + DMA in C_6H_6	(a) 0.00	8.5079	1.0937	1.0463	12.26	12.00	3.78	12.00	13.10 [13]
	(b) 0.30	4.48944	1.0719	1.0513	8.59	8.50		10.40	
	(c) 0.50	8.33645	1.0341	1.0406	11.28	11.32		9.34	11.86
	(d) 0.70	6.58776	1.0172	1.0132	9.76	9.74		8.27	
	(e) 1.00	3.27495	1.0097	1.0153	6.65	6.67	1.85	6.67	5.78
(III) THF + NMF in C_6H_6	(a) 0.00	11.15421	1.1153	1.0983	10.96	10.87	3.77	10.87	14.89
	(b) 0.30	7.30912	1.1660	1.1071	9.58	9.33		9.61	
	(c) 0.50	1.22845	1.1058	1.0933	9.19	9.14		8.77	13.15
	(d) 0.70	6.1258	1.0344	1.0282	8.81	8.78		7.93	
	(e) 1.00	3.27495	1.0095	1.0153	6.65	6.67	1.85	6.67	5.78
(IV) THF + DMF in C_6H_6	(a) 0.00	11.93042	1.0770	1.0414	13.19	12.97	3.81	12.97	12.46 [5]
	(b) 0.30	6.77217	1.0770	1.0234	9.92	9.67		11.08	
	(c) 0.50	2.8244	1.1675	1.1560	6.66	6.63		9.82	11.43
	(d) 0.70	3.08593	1.0749	1.0692	6.67	6.65		8.56	
	(e) 1.00	3.27495	1.0095	1.0153	6.64	6.67	1.85	6.67	5.78

Figure 5. The variation of τ_{jk}'s in ps with mole fraction x_j of THF for different binary polar mixtures of THF+amide at 25°C under 9.90 GHz electric field. (I) —■—; ···□··· NMA, (II) —●—; ···○··· DMA, (III) —▲—; ···△··· NMF and (IV) —★—; ···☆··· DMF for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of THF from Murthy *et al* (—) and ratio of slopes (···) respectively.
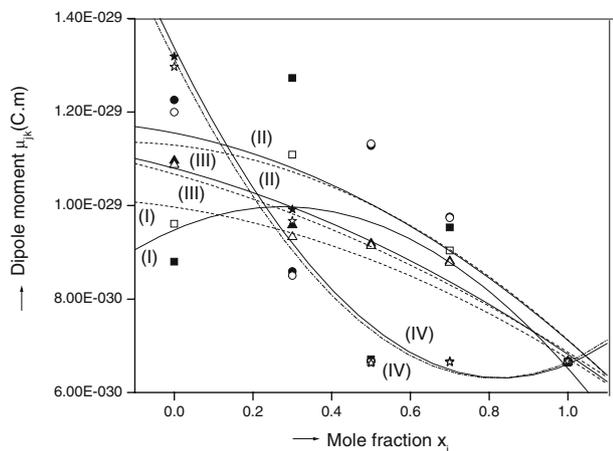
Figure 6. The variation of μ_{jk}'s in Coulomb·metre (C·m) with mole fraction x_j of THF for different binary polar mixture of THF+amide at 25°C under 9.90 GHz electric field. (I) —■—; ···□··· NMA, (II) —●—; ···○··· DMA, (III) —▲—; ··· △ ··· NMF and (IV) —★—; ···☆··· DMF for 0.0, 0.3, 0.5, 0.7 and 1.0 x_j of THF from Murthy *et al* (—) and ratio of slopes (···) respectively.

molecular association as evident from figures 7c and 7d may arise due to the interaction of +ve charge (δ^+) at the site of carbon or nitrogen atoms of the amides and fractional negative charge (δ^-) on the oxygen atom of THF molecule. Thus the dipole–dipole interaction occurs in such a way that the effective values of τ and μ of the rotating unit increase. Solute–solvent (monomer) molecular association may also happen due to the interaction of fractional +ve charge (δ^+) at the
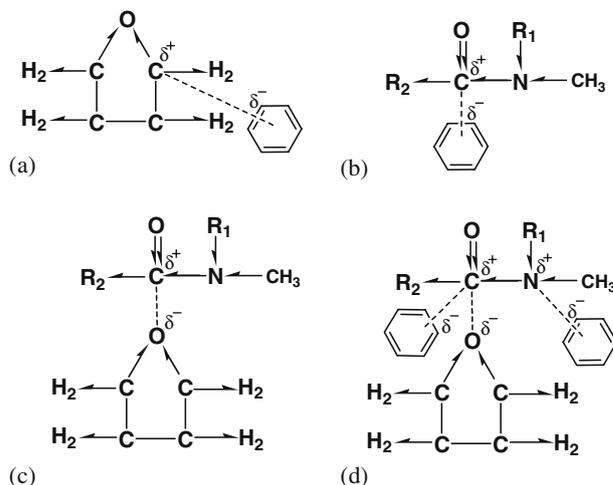
Figure 7. Theoretical dipole moments (μ_{theo}'s) from the available bond angles and bond moments (multiples of 10^{-30} C·m) of THF along with solute–solvent and solute–solute molecular associations. (**a**) THF–C_6H_6, (**b**) amide–C_6H_6, (**c**) amide–THF and (**d**) amide–THF–C_6H_6 (R_1 and R_2 are either H or CH_3).

site of carbon or nitrogen atom of the amide and C atom of THF with π delocalized electron cloud in the benzene molecule as seen in figures 7a and 7b respectively.

5. Conclusions

A simple approach is suggested to determine τ and μ of the binary polar mixture of THF with NMA, DMA, NMF and DMF dissolved in C_6H_6 by the conductivity measurement of solution under 9.90 GHz and 25°C to arrive at the solute–solutes and solute–solvent molecular association along with the structure of binary polar mixture under different states of molecular environment. The associational aspects are predicted from the stand point of τ_{jk}–x_j and μ_{jk}–x_j curves. It is evident that solute–solute (dimer) molecular association happens upto $x_j = 0.3$ and solute–solvent (monomer) molecular association happens thereafter upto $x_j = 1.0$ of THF for all systems except THF+DMA.

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