

## CHAPTER VI

# THEORETICAL RELAXATION TIME OF ASSOCIATED BINARY POLAR MIXTURE IN NON-POLAR SOLVENT

## 6.1 Introduction:

Study of dielectric relaxation phenomenon of a mixture of two polar liquids in dilute solution of a non-polar solvent under ultra-high frequency electric field is of considerable interest as it throws much light on the presence of various types of molecular associations. It also indicates the possibility of having optimum binary system corresponding to a desired physical property for a binary polar mixture of both associating components in a solvent. Schallamach (1946), from his study of temperature dependence of mixtures of polar molecules under radio frequency electric field, concluded that the dielectric relaxation in mixtures involves a rearrangement of relatively large region and if the components in a mixture are both associating or both non-associating, the dielectric behaviour appears to be correspond to a single relaxation process.

When a dipolar mixture is studied in a dilute solution its complex dielectric constant is represented by a weighted sum of the complex dielectric constants of individual components (Forest and Smyth 1965). Therefore the dependence of dielectric constants, dielectric loss and relaxation time on the concentration of the components should show linearity in the absence of solute-solute type of molecular association in the solution. The occurrence of polar molecular association results in relaxation time considerably higher than those for

unassociated molecules (Crossley 1971, Shama et al 1984, 1985, 1992). In these cases the dielectric behavior of the mixtures is mainly governed by the resulting molecular species.

Recently Yadav and Gandhi (1993) have proposed a theoretical relation for calculating relaxation time  $\tau_{mix}$  of binary polar mixture in dilute solution of non-polar solvent from the knowledge of the relaxation of the constituent component. Madan (1980, 1987) has also formulated two theoretical relations for computing relaxation time of binary polar mixture. The methods give the theoretical  $\tau_{mix}$  values which lie between the values of the individual components, but are unable to predict the  $\tau_{mix}$  values of mixtures where solute-solute associations occur. In this chapter we proposed a theoretical formulation for calculating relaxation times of polar mixtures of two associating liquids in non-polar solvent where solute-solute type of molecular associations really happened.

## 6.2. Theoretical Formulations:

Debye (1929) has shown that for systems, which can be characterized by a single relaxation time, the complex dielectric constant  $\epsilon^*$  is related to the relaxation time  $\tau$  by

$$\frac{\epsilon^* - \epsilon_\alpha}{\epsilon_0 - \epsilon_\alpha} = \frac{1}{1 + j\omega\tau} \quad \dots\dots\dots(6.1)$$

where  $\epsilon_\alpha$  and  $\epsilon_0$  are the dielectric constants of the polar component at infinite frequency and static field respectively. Substituting  $\epsilon^* = \epsilon' - j\epsilon''$ , we have from real and imaginary parts

$$\omega\tau = \frac{\epsilon''}{\epsilon' - \epsilon_\alpha} \dots\dots\dots(6.2)$$

If  $\tau_j$  and  $\tau_k$  are the relaxation times of polar components and  $\tau_{jk}$  that of their mixture in a non-polar solvent, from eq (6.2) we can write,

$$\omega\tau_j = \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\alpha ij}} \dots\dots\dots(6.3)$$

$$\omega\tau_k = \frac{\epsilon''_{ik}}{\epsilon'_{ik} - \epsilon_{\alpha ik}} \dots\dots\dots(6.4)$$

$$\omega\tau_{jk} = \frac{\epsilon''_{ijk}}{\epsilon'_{ijk} - \epsilon_{\alpha ijk}} \dots\dots\dots(6.5)$$

Now if the internal field of a polar mixture would not be much different from the internal field of its components, then it can be written as

$$\epsilon'_{ijk} = x_j \epsilon'_{ij} + x_k \epsilon'_{ik} \dots\dots\dots(6.6a)$$

$$\epsilon_{\alpha ijk} = x_j \epsilon_{\alpha ij} + x_k \epsilon_{\alpha ik} \dots\dots\dots(6.6b)$$

and  $\epsilon''_{ijk} = x_j \epsilon''_{ij} + x_k \epsilon''_{ik} \dots\dots\dots(6.6c)$

where  $x_j$  and  $x_k$  are mole fractions of the respective solutes in the polar mixtures.

It has been found in dilute solutions of polar solute in non-polar solvent that the dielectric constants and loss are proportional to the solute concentration (Hassel et al 1964) i.e.

$$\epsilon'_{ij} = \epsilon_i + a'_j \omega_j \quad \dots\dots\dots(6.7a)$$

$$\epsilon''_{\alpha ij} = \epsilon_i + a_{\alpha j} \omega_j \quad \dots\dots\dots(6.7b)$$

and  $\epsilon''_{ij} = a''_j \omega_j \quad \dots\dots\dots(6.7c)$

where  $\epsilon_i$  is the dielectric constant of the solvent.

Substituting eq. (6.6) in eq (6.5) and using eqs (6.3), (6.4) and (6.7) we obtain the relaxation time of polar mixture in dilute solution as

$$\tau_{jk} = \frac{\tau_j + x \tau_k a}{1 + x a} \quad \dots\dots\dots(6.8)$$

or  $\tau_{jk} = \frac{a'_j + x a'_k}{\frac{a'_j}{\tau_j} + x \frac{a'_k}{\tau_k}} \quad \dots\dots\dots(6.9)$

where  $x = \frac{x_k}{x_j}$  and  $a = \frac{a'_k - a_{\alpha k}}{a'_j - a_{\alpha j}}$

The relation (6.8) or (6.9) gives the  $\tau_{jk}$  values of polar mixtures which are average of the individual components. The relation is not fitted to the solutions of two associating polar mixtures where  $\tau_{jk}$  become higher than the average value due to solute-solute associations.

The assumption of linear variations of dielectric constants and loss with concentration, as given by eq (6.6), are not true for associating-associating polar mixtures. An examination of the dielectric constants and loss values of both associating binary polar mixtures in a non-polar solvent shows that the  $\epsilon'$  and  $\epsilon''$  values first decrease with the concentration and then increase whereas  $\epsilon''$  first increase and then decrease. We can represent these variations by the equations:

$$\epsilon'_{ijk} = x_j \epsilon'_{ij} + (1 - x_j) \epsilon'_{ik} \quad \dots\dots\dots(6.10a)$$

$$\epsilon''_{ijk} = x_j \epsilon''_{ij} + (1 - x_j) \epsilon''_{ik} \quad \dots\dots\dots(6.10b)$$

and  $\epsilon''_{ijk} = x_j \epsilon''_{ij} + (1 - x_j^2) \epsilon''_{ik} \quad \dots\dots\dots(6.10c)$

Substituting eqs (6.10) in eq (6.5) with eqs (6.3), (6.4) and (6.7) we get

$$\tau_{jk} = \frac{x_j \tau_j + (1 - x_j^2) \tau_k a}{x_j^2 + x_k^2} \dots\dots\dots(6.11)$$

$$\text{or } \tau_{jk} = \frac{x_j a_j'' + (1 - x_j^2) a_k''}{x_j^2 \frac{a_j''}{\tau_j} + x_k^2 \frac{a_k''}{\tau_k}} \dots\dots\dots(6.12)$$

where  $a = (a_k' - a_{\alpha k}) / (a_j' - a_{\alpha j})$

The eq (6.11) or (6.12) may be used to calculate the theoretical values of relaxation time of mixture of two associating polar liquids in a non-polar solvent in terms of individual relaxation time. For  $x_j = 1$  eq.(6.11) or (6.12) reduces to  $\tau_{jk} = \tau_j$  and for  $x_j = 0$  the equation gives  $\tau_{jk} = \tau_k$ . The slopes of the linear plots of dielectric constants or loss against concentration, as given by eq.(6.7), be used to calculate  $\tau_{jk}$  from eq. (6.11) or (6.12) with the advantage that individual errors in particular values of dielectric constants and loss are minimized.

### 6.3 Results and Discussion:

The simple theoretical relations for calculating  $\tau_{jk}$ , which are developed here, have been tested by six selected polar mixtures of two associating liquids containing forty one compositions in dilute solution of non-polar solvent using available dielectric relaxation data in the literature (Sharma et

al 1984, 1985, 1992). The theoretical values of  $\tau_{jk}$ , calculated by the eqs (6.9) and (6.12) using  $\tau_j$  and  $\tau_k$  of the individual components and the slopes  $a_j''$  and  $a_k''$  of the linear variations of dielectric loss against weight fraction, are placed in Table 6.1 along with  $a_j''$  and  $a_k''$ .

The development of suitable theoretical relation is of considerable importance for obtaining information about the relaxation phenomena of binary polar mixtures as well as for the formulation of adequate models of dielectric liquid relaxation. The eq.(6.8) or (6.9) has been developed with the assumption that the internal field of the pure component would not be different from the internal field of the mixture and  $\epsilon'_{ijk}$ ,  $\epsilon''_{ijk}$  and  $\epsilon'_{ijk}$ , can be expressed by a simple mixing relation as in eq.(6.6). This relation is not different from the relation recently developed by Yadav and Gandhi (1993). The  $\tau_{jk}$  values of the systems, calculated by eq.(6.9), are always within  $\tau_j$  and  $\tau_k$  values and are very close to the average values obtained by the equation  $\tau_{jk} = x_j \tau_j + x_k \tau_k$ , as shown in Table 6.1. These values show relatively large deviations from the experimental values (Table 6.1) for the systems studied. The relations to compute  $\tau_{jk}$  given by Madan (1980, 1987) also yield the values which lie between the  $\tau$  values of the individual components. These relations are not applicable to the polar mixtures of both associating solutes in dilute solution where  $\tau_{jk}$  values are expected to be higher than the average values due to increase in size in rotating unit as a

Table 6.1 Theoretical relaxation time ( $\tau_{jk}$ ) of binary polar mixtures in benzene\* with experimental ones at 15°C

Mixtures	$x_j$	$a''_j$	$a''_k$	Relaxation Time In P Sec			
				Computed from eq(6.9)	$\tau_{jk} = x_j \tau_j + x_k \tau_k$	Computed from eq(6.12)	Experimental $\tau_{jk}$
Dimethyl formide (DMF)	1.0			7.01	7.01	7.01	7.01
+ Methyl alcohol (MeOH)	0.9			6.96	6.91	7.98	7.87
	0.7			6.85	6.71	10.05	9.83
	0.5	10.9381	4.1223	6.70	6.51	11.67	12.87
	0.3			6.50	6.30	11.32	11.70
	0.1			6.20	6.10	8.16	8.94
	0.0			6.00	6.00	6.00	6.00
DMF	1.00			7.01	7.01	7.01	7.01
	0.95			6.84	6.83	7.34	7.43
	0.90			6.67	6.64	7.64	7.94
+ Acetone (AC)	0.70			5.98	5.91	8.47	10.73
	0.50	10.9381	4.7975	5.26	5.18	8.21	13.34
	0.30			4.52	4.45	6.70	8.76
	0.10			3.75	3.72	4.48	5.17
	0.00			3.35	3.35	3.35	3.35

Table 6.1 (continued)

Mixtures	$x_j$	$a''_j$	$a''_k$	Relaxation Time In P Sec			
				Computed from eq(6.9)	$\tau_{jk} = x_j \tau_j + x_k \tau_k$	Computed from eq(6.12)	Experimental $\tau_{jk}$
	1.0			7.01	7.01	7.01	7.01
DMF	0.9			6.89	6.91	8.28	10.78
+	0.7			6.67	6.72	10.12	8.94
Acetonitrile	0.5	10.9381	11.6772	6.47	6.53	10.49	8.47
(AN)	0.3			6.29	6.33	9.31	8.23
	0.1			6.12	6.14	7.21	7.78
	0.0			6.04	6.04	6.04	6.04
AC	1.0			5.08	5.08	5.08	5.08
+	0.7			5.07	5.07	7.42	7.98
Dimethylsul-	0.5	16.7589	9.8830	5.06	5.06	8.18	11.27
phoxide	0.3			5.05	5.05	7.33	4.46
(DMSO)	0.0			5.03	5.03	5.03	5.03

Table 6.1 (continued)

Mixtures	$x_j$	$a''_j$	$a''_k$	Relaxation Time in P Sec			
				Computed from eq(6.9)	$\tau_{jk} = x_j \tau_j + x_k \tau_k$	Computed from eq(6.12)	Experimental $\tau_{jk}$
	1.0			7.01	7.01	7.01	7.01
DMF	0.9			7.25	7.39	8.68	10.91
+	0.7	10.9381	10.3073	7.79	8.14	12.28	11.99
Tetramethylu- rea (TMU)	0.5			8.44	8.89	15.20	17.73
	0.3			9.22	9.64	15.62	15.47
	0.1			10.19	10.39	12.88	12.07
	0.0			10.77	10.77	10.77	10.77
	1.0			7.01	7.01	7.01	7.01
	0.9			7.14	7.20	8.49	7.56
DMF	0.7			7.44	7.58	11.52	9.19
+	0.5	10.9381	9.4159	7.77	7.96	13.63	10.72
Dimethylacet- amide (DMA)	0.3			8.17	8.33	13.45	9.83
	0.1			8.63	8.71	10.76	9.11
	0.0			8.90	8.90	8.90	8.90

\* For AC + DMSO mixture temperature is 25°C and solvent is carbon tetrachloride

result of solute-solute molecular association.

The internal field of polar mixture depends upon the dipole moments of its components and dipole-dipole interactions. Hence the internal field of associated polar mixtures in non-polar solvent may be expected to be different from the internal field of individual components. This change in internal field perhaps the reason of non-linear variation of dielectric constants and loss against concentration in the polar mixtures as given by eq.(6.10). The eq.(6.12) formulated with the above assumption, has been used to calculate  $\tau_{jk}$  of the systems. These values are close to the experimental values for most of the systems. The deviations of the theoretical  $\tau_{jk}$  values from the experimental ones, that have been appeared in case of some systems, are appreciably less than the deviations of  $\tau_{jk}$  values calculated by other methods. These theoretical  $\tau_{jk}$  values are plotted against mole fractions of one of the components in six binary mixtures containing both associated solute in dilute solution as shown in Fig 6.1. The figure shows that the relaxation time increases from  $\tau_j$  at  $x_k = 0.0$  as  $x_k$  is increased and reaching peak values decreases and finally drop to  $\tau_k$  at  $x_k = 1.0$  for all the mixtures. These curves (Fig 6.1) indicate the presence of associated solutes due to solute-solute molecular association and the molecular association is maximum through a small region of  $x_k$  which is consistent with the experimental results (Sharma et al 1984, 1985, 1992). In most of the systems the region of maximum

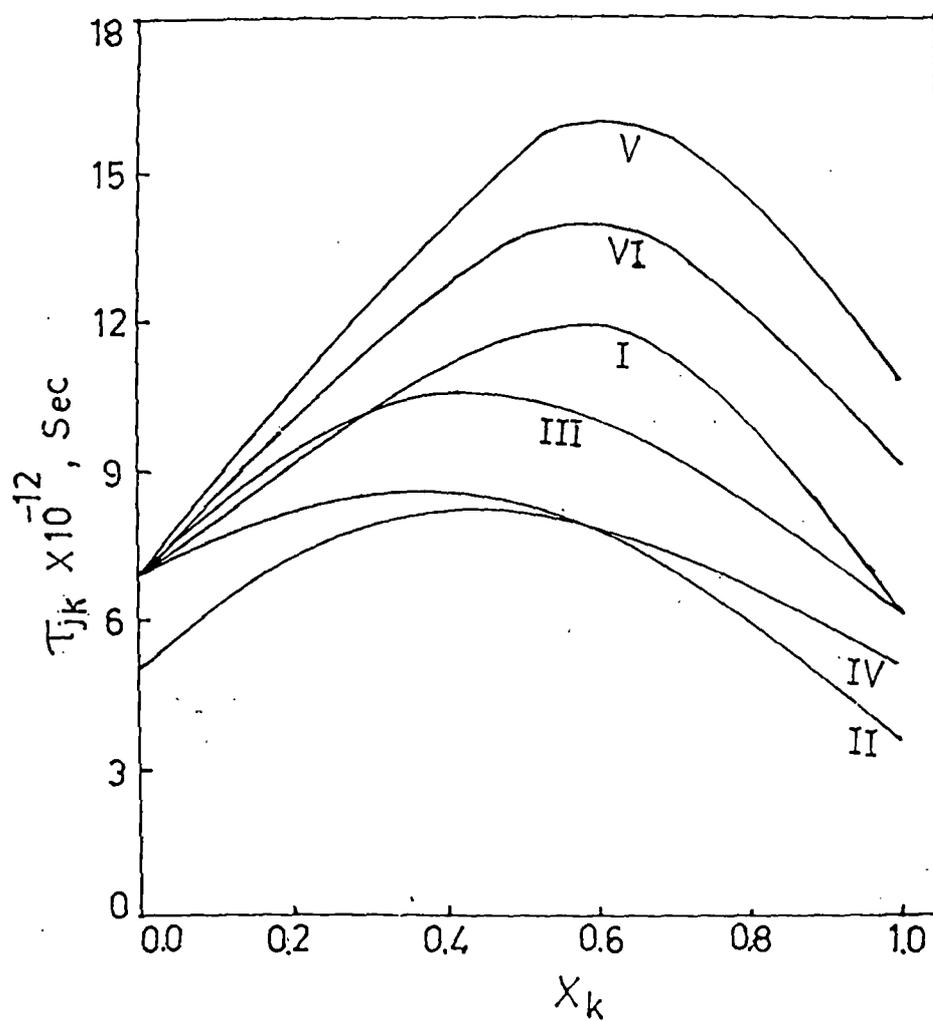


Fig. 6.1 - Variation of theoretical  $\tau_{jk}$  against mole fraction  $X_k$  (I DMF + MeOH, II DMF + AC, III DMF + AN, IV AC + DMSO, V DMF + TMU and VI DMF + DMA)

molecular associations as given by the theoretical curves agree well with results given by Sharma et al (1984, 1985, 1992) on the basis of experimental  $\tau_{jk}$ . It is thus obvious from the results that the predictions of  $\tau_{jk}$  values calculated by eq (6.12), which is based on Debye (1929) equation, for a polar mixture containing two associating liquids in a non-polar solvent is better than those by the other methods.

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