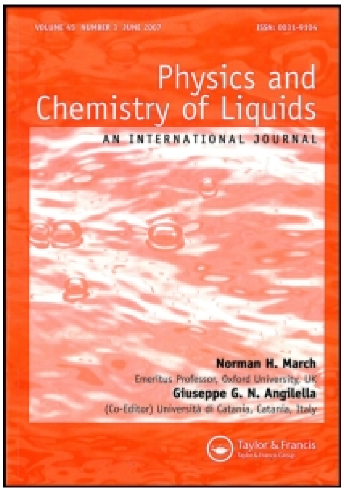

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Dielectric Relaxation Behaviour of Some Complexed Species—A Modified Equation for Relaxation Times

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Dielectric relaxion behaviour of four rigid substances and their complexes were investigated at microwave frequency of 9.8 GHz and at varying temperatures. A modified equation for calculating apparent relaxation time of complexed species having short range interactions was suggested. The apparent relaxation time values so calculated were compared with the experimentally observed values of the complex systems. A good agreement has been reached for the systems having nearly negligible distribution, exhibiting a Debye type dispersion.

INTRODUCTION

The single frequency methods[1–3] for determining relaxation time in the case of rigid polar molecules give an average effect representing the overall relaxation. However, Higasi, Koga and Nakamura method[4] enables one to resolve the dispersion into separate relaxation processes, associated with group and molecular rotations. The assessment based on aforesaid techniques gives valuable informations, about the qualitative behaviour of the molecule under applied field. Schallamach's[5] investigations of binary mixtures as a function of temperature, at a fixed frequency reveal that the dielectric relaxation involves relatively large regions, indicating single relaxation process in the liquid, provided that the polar components are both associative or both non-associative. Several workers[6–9] have reported two relaxation process in binary mixtures of components having sufficiently different relaxation times. Shukla *et al.*[10] have studied various H-bonded complexes (N—H—N) within polystyrene matrix and have interpreted their results in terms of enthalpy parameters.

Recently Madan[11] proposed an empirical relation for apparent relaxation time (τ_a) of non-associative binary mixtures comprised by pyridine, quinoline and isoquinoline molecules, in *n*-heptane and benzene solutions. Comparison of experimental relaxation time (τ) of binary mixtures with τ_a calculated using the proposed relation show an agreement. Madan's relation has given satisfactory results for non-associative systems, in which short range interactions may be neglected. However, if the components are of associative nature, i.e. capable of forming complexes through H-bonding or charge transfer, this relation is needed to be ascertained in the light of different dipolar units associated, in the solution and to modify it in order to take into account the dipolar rotations. With this in view dielectric measurements on four rigid molecules, e.g. pyridine, quinoline, pyrrole and indole and their complexes in dilute solutions were made. A modified relation was subsequently suggested and the apparent relaxation times were determined using the modified equations. Generally a good agreement was observed in the experimental and calculated τ values and also the corresponding thermodynamical parameters.

THEORY

The study of relaxation behaviour of binary mixtures, capable of forming complexes as well as developing adequate models to fit in the experimental relaxation data, is of considerable importance. For non-associative type of systems comprising of rigid polar molecules in non polar solvents, the apparent relaxation time τ_a was given by

$$\frac{1}{\tau_a} = \sum_i \frac{A_i}{\tau_i} \tag{1}$$

Where A_i represents the effect of shape, size, viscosity fractional volumes, solute-solvent interactions and factors influencing dipole reorientation of i^{th} constituents. Neglecting the solute-solvent interactions in the dilute solution investigations and considering that the contribution of a particular relaxation depends upon squared dipole moments (μ_i), then A_i will be

$$A_i = \frac{C_i \mu_i^2}{\sum_i C_i \mu_i^2}$$

Here C_i represents the parameter involving all effects except that of dipole moment.

For non-associative, simple rigid binary mixtures Eq. (1) reduces to

$$\frac{1}{\tau_a} = \frac{C\mu_1^2}{(C\mu_1^2 + \mu_2^2)\tau_1} + \frac{\mu_2^2}{(C\mu_1^2 + \mu_2^2)\tau_2} \tag{2}$$

C being the molar concentration ratio (C_1/C_2) of the two components 1 and 2, corresponding dipole moment values are μ_1 and μ_2. C is observed to be unity for molecules of comparable size.

The dipole moment of the binary complex formed in the solutions of molar concentration ratio 1 : 1 may be represented by the resultant vector of the two component vectors (shown in Figure 1) as

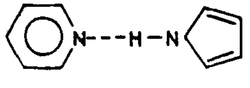
$$\mu_C^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\varphi \tag{3}$$

already suggested by Magee and Walker[12] in case of C-H—N bond complexes of amine molecules with chloroform, φ being the angle between the vectors of such bonds. The term '$2\mu_1\mu_2 \cos\varphi$' represents the association factor between the single systems.

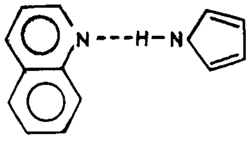
If the relaxation time of the binary complexed species arising from the H-bonding between the units under ideal conditions be considered as an approximate sum of the relaxation times of the individuals as has been observed experimentally in several cases, the apparent relaxation time in terms of the associated moments for the system of binary complexes may be represented by the following modified equation.

$$\begin{aligned}\frac{1}{\tau_a} &= \frac{1}{\tau_1}\,\frac{C_1\mu_1^2}{C_1\mu_1^2 + C_2\mu_2^2} + \frac{1}{\tau_2}\,\frac{C_2\mu_2^2}{C_1\mu_1^2 + C_2\mu_2^2} \\ &\quad + \frac{1}{\tau_1 + \tau_2}\cdot\frac{2\sqrt{C_1C_2}\,\mu_1\mu_2}{C_1\mu_1^2 + C_2\mu_2^2}\cos\varphi\end{aligned} \tag{4}$$

Since the systems considered here are of associative nature, capable of forming complexes, the third term of the proposed relation would represent association factors in terms of individual relaxation times and dipole moments. This is analogous to the previous equation except that a term



Pyridine • Pyrrole



Quinoline • Pyrrole

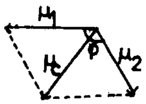
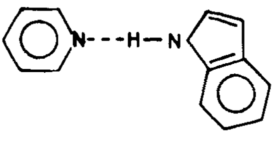
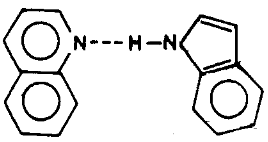


Figure 1



Pyridine • Indole



Quinoline • Indole

representing the complexed species has been added to provide an overall effect on the apparent relaxation time of the system under investigation. Perhaps, the best suitable form in terms of the associative dipoles having moments μ_1 and μ_2 could be represented by Eq. (4).

The concentration factor C_i is considered as $\sqrt{C_1 C_2}$ in the association term, which accounts for the contribution of short range interactions substituting C in place of C_1 and C_2, the above equation reduces to

$$\frac{1}{\tau_a} = \frac{1}{C\mu_1^2 + \mu_2^2}\left[\frac{C\mu_1^2}{\tau_1} + \frac{\mu_2^2}{\tau_2} + \frac{2\sqrt{C}\,\mu_1\mu_2}{\tau_1 + \tau_2}\cos\varphi\right] \tag{5}$$

The apparent relaxation time τ_a of the complexed species may be estimated using Eq. (5) and compared with the experimental data.

EXPERIMENTAL

Four rigid molecules viz. pyridine, quinoline, pyrrole, indole and their binary complexes were investigated in dilute solutions of non polar solvent cyclohexane. The binary complexes are

i) Pyridine + Pyrrole
ii) Quinoline + Pyrrole
iii) Quinoline + Indole
iv) Pyridine + Indole

The ratio of molar concentration of the component molecules was 1:1 in cyclohexane over the temperature range 293–323 K. Permittivity data (ε' and ε'') for these systems have been measured at x-band (9.8 GHz) by Roberts and von Hippel[13] technique, later modified by Dakin and Works.[14] The static dielectric constant ε_0 at 300 KHz was measured using RLO9 dipolemeter, based on Heterodyne beat principle. The refractive indicies were measured using Abbe refractometer.

RESULTS AND DISCUSSION

The relaxation parameters of individual molecules, calculated using G. Krishna method[1] (τ_G), Higasi method[2] (τ_{OH}) and Fröhlich method[3] (τ_F), distribution function (α) and the dipole moment (μ) values over the temperature range investigated have been reported in Table I. Experimental relaxation parameters, distribution function (α) of binary complexes and their corresponding apparent relaxation times (τ_a) calculated using the proposed relation have been given in Table II. The structures of complexes formed are

TABLE I

Relaxation times: τ_G, τ_{OH}, τ_F, distribution parameter (α) and dipole moment μ of individual molecules at 9.8 GHz

Substance	Temp. K	τ_G ps	τ_{OH} ps	α	τ_F ps	μ D
Pyridine (0.089–0.169)†	293	3.1	3.6	0.07	3.8	2.28
	303	2.7	3.8	0.02	3.5	2.18
	313	2.5	3.4	0.02	3.0	2.11
	323	2.3	3.0	0.04	2.8	2.09
Quinoline (0.105–0.281)†	293	8.7	10.1	0.08	7.7	1.99
	303	7.7	9.5	0.05	6.9	1.74
	313	6.9	9.3	0.04	6.2	1.54
	323	6.3	8.9	0.04	5.5	1.40
Pyrrole (0.124–0.228)†	293	5.5	5.2	0.00	5.8	1.31
	303	4.8	4.8	0.01	5.5	1.33
	313	4.5	4.4	0.03	5.0	1.29
	323	4.1	4.1	0.03	4.3	1.32
Indole (0.149–0.183)†	293	12.7	9.4	0.11	11.5	2.13
	303	11.6	9.3	0.10	10.0	2.00
	313	11.1	8.7	0.02	9.1	1.83
	323	9.0	8.4	0.05	7.9	1.75

† Weight fraction range.

TABLE II

The experimental relaxation times (τ) along with apparent time (τ_a) values calculated using Eq. (5)

	Gopalakrishna method		Higasi method			Fröhlich method	
Temp. K	τ_G ps	τ_a ps	τ_{OH} ps	α	τ_a ps	τ_F ps	τ_a ps
	Pyridine + *Pyrrole* (0.082–0.153,† 1.167‡						
293	7.1	5.1	6.6	0.03	6.1	8.6	6.4
303	6.5	4.6	6.3	0.02	—	7.7	6.0
313	5.9	4.3	6.1	0.00	5.9	6.8	5.2
323	5.1	4.0	5.9	0.00	5.3	6.0	4.9
	Quinoline + *Pyrrole* (0.071–0.135),† 1.645‡						
293	12.2	13.9	14.1	0.01	15.3	14.3	12.7
303	10.5	12.5	12.6	0.03	14.5	12.3	12.0
313	8.8	11.4	11.8	0.01	13.3	10.8	11.0
323	8.0	10.3	11.0	0.01	11.8	9.0	9.8
	Quinoline + *Indole* (0.128–0.150),† 1.032‡						
293	20.2	20.3	21.0	0.02	19.6	21.6	18.3
303	18.6	18.4	19.8	0.08	18.6	18.6	16.4
313	16.2	17.1	17.7	0.07	17.1	14.7	14.9
323	13.6	15.3	16.0	0.07	16.5	12.5	13.2
	Pyridine + *Indole* (0.128–0.159),† 0.686‡						
293	10.4	8.1	10.0	0.16	9.2	11.3	9.7
303	8.0	7.0	9.6	0.16	8.7	10.1	9.1
313	6.6	6.1	8.8	0.17	7.4	9.0	7.4
323	5.7	5.5	8.0	0.23	7.3	8.4	5.4

† Weight fraction range.

‡ C(mole fraction ratio value, C_1/C_2).

TABLE III

The free energy (ΔF_ε), enthalpy (ΔH_ε) and entropy (ΔS_ε) of activation evaluated using τ_{OH} and corresponding τ_a values

	Temp.	ΔF_ε(KJ/mol)		ΔH_ε(KJ/mole)		$-\Delta S_\varepsilon$(Jmol^{-1} deg^{-1})	
Complex	K	[τ_{OH}]	[τ_a]	[τ_{OH}]	[τ_a]	[τ_{OH}]	[τ_a]
Pyridine + Pyrrole	293	6.38	6.35	1.91	1.87	15.26	15.29
	303	6.49	—			15.16	—
	313	6.62	6.53			15.05	14.89
	323	6.74	6.45			14.95	14.18
Quinoline + Pyrrole	293	8.23	8.43	4.91	4.79	11.33	12.42
	303	8.23	8.58			10.96	12.50
	313	8.33	8.64			10.93	12.30
	323	8.41	8.60			10.83	11.80
Quinoline + Indole	293	9.21	9.04	5.63	5.63	12.22	11.64
	303	9.37	9.21			12.34	11.82
	313	9.39	9.30			12.01	11.73
	323	9.42	9.50			11.73	11.98
Pyridine + Indole	293	7.40	7.19	5.98	5.80	4.85	4.74
	303	7.55	7.30			5.18	4.95
	313	7.57	7.12			5.08	4.22
	323	7.56	7.31			4.89	4.67

also depicted. The dipole moments of individual molecules have been determined using Koga's method.[15] The thermodynamical parameters reported in Table III were evaluated from the τ_{OH} values and corresponding τ_a values using Eyring's theory of rate process.[16]

The observed relaxation times τ_G, τ_{OH} and τ_F of individual molecules have been found, in general to be in good agreement with each other. The observed τ values for pyridine (3.8 ps) and quinoline (9.5 ps) at 303 K, are found to be in good agreement with τ values of 3.5 ps and 8.8 ps respectively, reported earlier by Madan.[11] The relaxation time of pyrrole (4.8 ps) at 303 K appears to be longer than the earlier reported values[6] of 2.0 ps. The longer τ of pyrrole may arise from its self-associative nature, earlier been pointed out by Happe.[9] The observed relaxation time in the case of indole (11.6 ps) at 303 K, exhibits good agreement with the reported value of 11.0 ps.[6]

The complexed species observed in this study exhibit nearly zero values of distribution parameter (α), indicating the rigid behaviour of the binary complexes formed due to N-H—N bonding. The exception is the case of pyridine + indole complex for which α lies in the range of 0.16 to 0.23, slightly higher than the ranges of other complexed species. α values range for pyridine + pyrrole, quinoline + pyrrole and quinoline + indole are

(0.03–0.00), (0.03–0.01) and (0.08–0.01) respectively. The higher value of α suggests slight flexibility in the relaxation behaviour of pyridine + indole complex. It may be considered due to some type of associated behaviour perhaps exhibited by the indole molecules.

The average relaxation times τ_G, τ_F and τ_{OH} of the complexed species investigated were found to be in agreement with each other. All the three relaxation times are observed to be longer than those of component molecules. However, the τ_{OH} values were observed shorter in the case of pyridine complexes than the τ_G and τ_F values. At 303 K τ_G, τ_F and τ_{OH} values of pyridine + pyrrole complex are 6.5 ps, 7.7 ps and 6.3 ps respectively. Similarly the τ values of quinoline + pyrrole, quinoline + indole and pyridine + indole complexes are (10.6, 12.3 and 12.6) ps, (19.8, 18.6 and 19.8) ps and (8.0, 10.1 and 9.6) ps respectively.

The apparent relaxation time calculated using relaxation time and dipole moment values of component molecules, from the proposed relation [Eq. (5)] may be compared well with the experimentally observed values in all the binary systems investigated, though in some cases they are little higher and lower, viz. complex quinoline + pyrrole and pyridine + indole respectively. This may be attributed to the non unity mole fraction ratios (Table II) in these binary systems. The close agreement exhibited between the calculated and observed τ values indicate the validity of the proposed relation for the apparent relaxation time (τ_a) for the systems having short range interactions and intramolecular hydrogen bonding.

The thermodynamical parameters, e.g. free energy (ΔF_ε), enthalpy (ΔH_ε) and entropy (ΔS_ε) of activation for relaxation process, reported in Table III were found to be in agreement of those investigated by Shukla *et al.*[10] The free energy of activation has been found to increase with temperature in general. The entropies, ΔS_ε, observed are low as would be expected owing to small rigid systems in dilute solutions. The enthalpies, ΔH_ε calculated from the two relaxation times are found to be in good agreement.

CONCLUSION

It may be concluded that the modified equation explains the behaviour of associative, intermolecularly active and strongly H-bonded binary complex systems. The values calculated from the proposed relation compare well with the observed values, for complexes exhibiting a Debye type dispersion. It deviates in the system having distribution in relaxation. We, however suggest further investigations in order to establish the proposed model for relaxation behaviour of complexed species.

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