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DIPOLAR INCREMENTAL AND DIELECTRIC RELAXATION STUDIES OF TETRAHYDROFURAN WITH CYCLOHEXANOL

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Abstract:

The experimental values of the dipolar increment of the complex of tetrahydrofuran with cyclohexanolin dilute solutions of benzene have been measured at a temperature of 303 K. Dipolar incremental values of the systems were calculated using Huyskens method based on Onsager′s theory. Some results related to the dipole moment enhancement (Δμ) caused by hydrogen bond formation between donor and acceptor molecules are discussed.In continuation of the dipolar incremental studies the dielectric relaxation studies by frequency domain were carried out. By using Higasi method and Cole –Cole method, Higasi parameters and relaxation time τ were found .Eyring relations were used to compute the activation free energy. The dielectric relaxation parameters obtained have been used to understand the change in molecular association and size of the complex molecules formed with change in concentration of one component.

Key Words: H-Bonding, Complexation, Dipolar Increment, Dipolar Relaxation, Polarization Effect & Proton Donor and Proton Acceptor

1. Introduction:

Dipole moment is like one of the physical properties such as melting point, boiling point etc. of compounds.By the study of dipole moment of complex; it is possible to obtain information on inductive effects, resonance effects, shape of molecule (stereo chemical and conformational), hydrogen bonding, orientation etc. Thephysical properties of a compound depend mainly upon the kind ofbonds between atoms together in the molecule.Alcoholsmolecules are held together by hydrogenbonds, so they are highlyassociated liquids. Hydrogen bonding is a strong kind of dipole–dipole attraction in which a hydrogen atom serves as a bridgebetween two electronegative atoms, holding one by a covalent bondand the other by purely electrostatic forces.The most importantcharacteristic of the hydrogen bond is the increase in the distance O–Haccompanied by the enhancement of the bond moment Δμ [1].

Thedipole moment μ_{ab} of the complex does not exactly correspond to thevector addition of the momentsμ_a and μ_b of the separated compoundsdue to charge separation [2]. The nature of the complex is given by thevalue of the dipole moment since the dipolar increment is a function of ΔpK_a [3]. The dipolar increment in O–H…O complexes is due toeither polarization effect [4] or charge transfer effect [5] or partialproton transfer effect [6] or complete proton transfer effect [8].

Dielectric relaxation times [8, 9] give the confirmation about the intramolecular rotations and steric hindrance offered by the intramolecular association and the environment to the group rotations. The traditional methods of dielectric permittivity were based on the measurements in the frequency domain [10, 11]. Wereport here the results of our investigation on the hydrogen bonded complexes of tetrahydrofuran with cyclohexanoldilute solutions of benzene.

2. Materials and Methods:

The dielectric constants were measured [12] at 1 kHz using aVLCR-7meter supplied by Vasavi Electronics, India. The temperaturewas maintained at 308±1 K with the help of a water circulatingthermostat. The refractive indices were measured with Abbe′srefractometer. Densities were determined using a 10 ml specificgravity bottle and a K-Roy micro balance. BD Hanala variety of tetrahydrofuran and cyclohexanol were obtained from Sisco Research Laboratories, Limited, Mumbai, were distilled and the distillates collected at their boiling temperatures and used. The uncertainties indielectric constants, refractive indices and densities were ± 0.0005, ± 0,0002 and 0.0001 g/cc respectively.

3. Theory:

The permanent dipole moment μ_a of the proton donor in the liquidphase was computed from the dielectric constant ε_0 of the solution inbenzene. Onsager′s relation for the dipole moment of a liquid in termsof the dielectric constant takes care of the reaction field of theenvironment and leads to an equation [13]

$$\langle \bar{\mu}_{ab}^2 - \bar{\mu}_b^2 \rangle \frac{C_A}{C_B} + \langle \bar{\mu}_b^2 \rangle = \frac{9kT}{4\Pi N_A} \left[\frac{(\varepsilon_0 - n_D^2)(2\varepsilon_0 + n_D^2)}{\varepsilon_0 (n_D^2 + 2)^2} \frac{1}{C_B} - \frac{C_S}{\bar{C}_S} \frac{1}{C_B} \frac{(\varepsilon_S - n_{DS}^2)(2\varepsilon_S + n_{DS}^2)}{\varepsilon_S (n_{DS}^2 + 2)^2} \right] \quad (1)$$

Where C_a, C_b and C_{ab} are the actual concentrations of the entities ofproton donor, proton acceptor and the 1:1 complex, C_s is the actualconcentration of the solvent , $\bar{C}_S$ is its concentration in mol m^{-3} in the pure state, μ_b is the dipole moment of the proton acceptor and μ_{ab} is the dipole moment of 1: 1 complex. If the formal concentration C_B ofthe proton acceptor is far greater than the formal concentration C_A ofthe proton donor .the equilibrium constant for 1:1 complexation and ifthe solvent has zero dipole moment, then Eq. (1) reduces to

$$\langle \bar{\mu}_{ab}^2 - \bar{\mu}_b^2 \rangle \frac{C_A}{C_B} + \langle \bar{\mu}_b^2 \rangle = \Omega_B \quad (2)$$

The experimental values of dielectric constants, refractive indices,(C_A/C_B) and for different concentrations of the systems are given inTable 1.The linearity of (C_A/C_B) versus Ω_B shows the existence of 1:1complexes and the absence of higher order complexes. When a protondonor (a) of dipole moment μα forms a H-bond with a proton acceptor (b) of dipole moment μ_b, the direction of μα and μb with respect toA–H…B axis can be defined as θα and θb respectively. If θα and θ_b differfrom zero, one can define the azimuth angle ϕ, which describes therotation position of μ_b around the hydrogen bond with respect to theplane formed by this bond and μα, the dipolar increment due tocomplexation can be given vectorially as [14]

$$\Delta\mu = [\mu_{ab}^2 - \mu_a^2 \sin^2\theta_a - \mu_b^2 \sin^2\theta_b - 2\mu_a\mu_b \sin\theta_a \sin\theta_b < \cos\varphi >]^{\frac{1}{2}} - \mu_a \cos\theta_a - \mu_b \cos\theta_b \quad (3)$$

The computed values of static permittivity, permittivity at optical frequency, density and Ω_B are given in table 1. Bond angles, dipole moment and Δμof 1:1complexes are given in table 2.

Relaxation time and thermodynamic parameters were obtained from the values of dielectric constants. In this investigation relaxation time of liquids is determined by two different methods which are given below.

(a) Higasi method provides multiple relaxation times, one for overall rotation and another one for group rotation. Higasi [15] assumed a linear variation of ε_0, ε', ε'' and ε_∞ with weight fraction w_2 of the solute, and hence one can write

$$\varepsilon_0 = (\varepsilon_1 + a_0 w_2), \varepsilon' = (\varepsilon_1 + a' w_2), \varepsilon'' = (a'' w_2), \varepsilon_\infty = (\varepsilon_{1\infty} + a_\infty w_2) \quad (4)$$

Where a_0, a', a'' and a_∞ are constants known as Higasi parameters.

Higasi [16, 17] derived a relation connecting τ_0 and α

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

Where τ_0 is the most probable relaxation time, α is distribution parameter, ω is the angular frequency and

$$A = a''(a_0 - a_\infty), B = (a_0 - a')(a' - a_\infty) - a''^2, C = (a' - a_\infty)^2 + a''^2 \quad (6)$$

The Debye equation in terms of a_0, a', a'' and a_∞ yields two independent equations [18].

$$\tau_1 = \frac{a''}{\omega(a' - a_\infty)} \quad , \qquad \tau_2 = \frac{a_0 - a'}{\omega a''} \quad (7)$$

(b) In Cole –Cole method the measured values of permittivity and dielectric loss at microwave frequency, static permittivity and permittivity at optical frequency were fitted in a complex plane plot with a depressed circular arc. The angle made by the diameter drawn through the center from the ε_∞point and the x-axis is given by $(\alpha\pi/2)$. From the Cole-Cole plot the relaxation time τ can be found out using the equation [19].

$$(\omega\tau)^{1-\alpha} = \left(\frac{v}{u}\right) \quad (8)$$

Where α is the distribution parameter, ω is the angular frequency, v is the distance between ε_0 and experimental point on the Cole-Cole plot, u is the distance between ε_∞ and that point on the Cole-Cole plot.

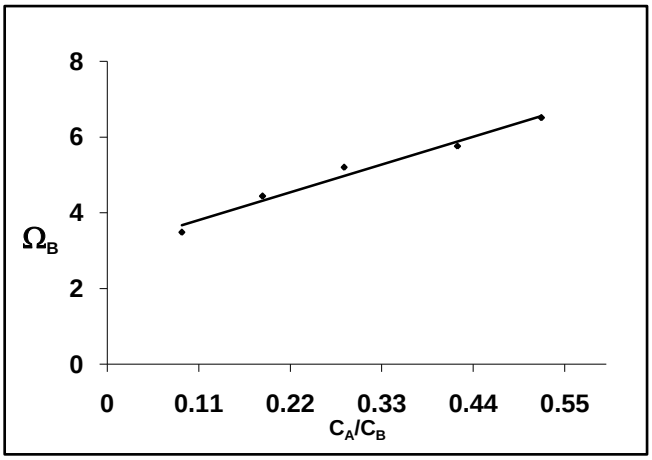
Eyring relations were used to compute the activation free energy from the equations which are given below [20].

$$\tau = \left(\frac{h}{kT}\right)\exp\left(\frac{\Delta F_\tau}{RT}\right) \quad , \qquad \eta = \left(\frac{N_A h}{V}\right)\exp\left(\frac{\Delta F_\eta}{RT}\right) \quad (9)$$

Where N_A, k, h, R, V and T are Avogadro's number, Boltzmann constant, Planck's constant, Universal gas constant, molar volume of the mixture and temperature in Kelvin respectively. ΔF_τ refers to the activation free energy due to relaxation mechanism and ΔF_η stands for activation free energy due to viscosity. Values of Higasi's parameters, Relaxation time, Distribution parameter, Activation energy and viscosity, values of enthalpy and entropy for various ratios of for different temperature are given in the tables 3-6.

C_A m/l	ε_0	ε_∞	ρ g/cc	$\Omega_B D^2$
0.086	*2.6529*	*2.2118*	*0.8629*	*3.48*
0.180	*2.7745*	*2.2106*	*0.8647*	*4.44*
0.274	*2.8717*	*2.2088*	*0.8655*	*5.20*
0.405	*2.9446*	*2.2076*	*0.8672*	*5.76*
0.502	*3.0418*	*2.2052*	*0.8680*	*6.51*

Table 1: Variation of static permittivity, permittivity at optical frequency, density and Ω_B with the formal concentration CB = 0.962 m/l



Systems	θ_a degrees	θ_b degrees	μ_a D	μ_b D	μ_{ab} D	$\Delta\mu$ D
Tetrahydrofuran + cyclohexanol	28°	0°	1.86	1.75	3.12	-0.40

Table 2: Bond angles, dipole moment and Δμ of 1:1complexes

Temp*(K)*	Ratio A:B	ε_o	ε'	ε''	ε_∞
303	1:0	2.6286	2.5981	0.1023	2.2147
	2:1	2.7502	2.5503	0.2298	2.1928
	1:1	2.7745	2.5241	0.2576	2.1910
	1:2	2.7502	2.5334	0.2212	2.1975
	0:1	2.8231	2.6246	0.1358	2.1969
313	1:0	2.6172	2.5790	0.1146	2.1668
	2:1	2.7416	2.5935	0.2167	2.1827
	1:1	2.7665	2.5171	0.1996	2.1845
	1:2	2.7416	2.5287	0.2193	2.1916
	0:1	2.7665	2.6025	0.1359	2.1904
323	1:0	2.6320	2.5861	0.1233	2.1609
	2:1	2.7340	2.5639	0.2128	2.1809
	1:1	2.7595	2.5155	0.2131	2.1756
	1:2	2.7340	2.5202	0.2042	2.1845
	0:1	2.7340	2.5988	0.1318	2.1842

Table 3: Values of Higasi's parameters

Ratio A:B	ΔH_τ J/mole	ΔS_τ J/mole	ΔH_η J/mole	ΔS_η J/mole
1:0	-5244	44.72	13334	-4.19
2:0	4241	21.07	14380	-7.46

1:1	1157	33.23	14108	-5.92
1:2	4337	22.68	14050	-4.54
0:1	2850	20.28	16349	-12.06

Table 4: Values of enthalpy and entropy for various ratios

Temp (K)	Ratio A:B	Relaxation Time (ps)			
		Higasi			Cole-Cole
		τ_0	τ_1	τ_2	τ
303	1:0	4.68	4.70	4.85	4.26
	2:1	12.12	11.39	14.12	11.25
	1:1	14.59	13.80	15.77	13.68
	1:2	13.04	11.74	15.91	12.05
	0:1	6.32	5.54	23.73	5.52
313	1:0	4.82	4.88	5.41	4.40
	2:1	9.49	9.27	11.09	8.77
	1:1	13.92	10.75	20.28	12.63
	1:2	12.90	11.64	15.76	11.87
	0:1	6.14	5.79	19.58	5.37
323	1:0	4.98	5.09	6.04	4.54
	2:1	10.39	9.84	12.98	9.54
	1:1	13.67	11.23	18.59	12.48
	1:2	12.67	10.91	17.00	11.54
	0:1	5.49	5.59	16.66	4.82

Table 5: Values of Relaxation time by Higasi and Cole-Cole method

Temp (K)	Ratio A:B	Distribution Parameter		Activation Energies (KJ/mol)		η x 10^{-4} (P)
		Higasi	Cole-Cole	ΔF_τ	ΔF_η	
		α	α			
303	1:0	0.005	0.019	8.60	12.08	5.41
	2:1	0.066	0.092	11.06	12.12	5.42
	1:1	0.042	0.072	11.45	12.34	5.88
	1:2	0.095	0.123	11.25	12.68	6.69
	0:1	0.408	0.422	10.81	12.71	6.73
313	1:0	0.018	0.032	8.78	11.98	4.44
	2:1	0.051	0.072	10.50	12.05	4.50
	1:1	0.197	0.226	11.45	12.20	4.74
	1:2	0.094	0.124	11.23	12.63	5.58
	0:1	0.341	0.357	10.62	12.55	5.38
323	1:0	0.033	0.047	8.97	12.00	3.50
	2:1	0.082	0.106	10.77	11.97	3.78
	1:1	0.157	0.187	11.39	12.23	4.14
	1:2	0.137	0.167	11.24	12.58	4.71
	0:1	0.297	0.312	10.37	12.47	4.46

Table 6: Values of distribution parameter, Activation energy and Viscosity

4. Results and Discussions:

The variation of Ω_B with C_A/C_B is shown in the figure. The values of $\overline{\mu}_{ab}$ and $\overline{\mu}_b$ are obtained from the slope and the intercept of the straight line graph. Assuming that the dipole moment of the complex is along the axis of the H-bond, we have taken $\theta_B = 0^o$ for THF and θ_A is assumed to be 28^o for cyclohexanol.

The static permittivity values are increasing with the increasing concentration of donors. This may be due to the existence of hetero interaction between the liquids [21, 22]. This hetero interaction leads to an enhancement in the dipole moment. The dipolar incremental studies reveal the type of interaction occurring between the proton donor and acceptor [23].

The dipolar increments ($\Delta\mu$) is very low and also negative. This implies the absence of charge transfer effects. The interaction due to electrostatic effects does not contribute significantly to the dipole moment incrementof the complex [24].Hence it is clear that the polarization effect alone is responsible for the dipolar increment in the complex due to hydrogen bonding between donors and acceptors.

The reason for the negative value of excess dipole moment may be due to solvent induced medium effect (SIME)[25]. Approximately straight lines have been obtained for the plot of Ω_B with C_A/C_B and this indicates the formation of 1:1 complex [26]. This indicates that the of 1:1complexation exist and rules out the possibility of higher order complexes like 1:2, 2:1 etc.

The results show that τ_o values obtained by Cole-Cole are lower than the values obtained by Higasi method. This may be attributed by the non- rigid behavior of the solute molecules [27]. In alcohol rich regions the values of τ_2 is greater than τ_1 for all the temperatures,it is because the intermolecular relaxation time is greater than the intramolecular relaxation time [28].

For moleculesif $\tau 1 = \tau_2$ which may attributed due to the rigid behavior of molecules [29]. Tetrahydrofuran being a rigid molecule our result shows that τ_1 differ from τ_2 by a little disparity. It may be due to a small but appreciable absorption in the high frequency region [30]. The above discussion is also supported for tetrahydrofuran by the small value of distribution parameter in the range 0.005 to 0.023.For tetrahydrofuran the relaxation time increases with increase in temperature.. It may be due to the expansion in volume of the tetrahydrofuran molecules with rise in temperature.

The decrease of distribution parameter with increase of temperature is observed for cyclohexanol in benzene, this may be explained as due to the fact that at higher temperature molecular rotation of the solute molecules become faster and uniform in solution. The faster rotation may be due to the smaller size of the molecule or due to the viscous effect [31]. The results show that for all the temperatures, the difference between $\tau 1$ and $\tau 2$ is appreciable and values of τ_2 are greater than τ_1. The difference between two relaxation times is explained as due to the existence of intramolecular relaxation process in addition to the overall relaxation process. [32].

It is observed that the value of τ_2 in alcohol decreases with the addition of tetrahydrofuran. This behavior is normal in the sense that the tetrahydrofuran molecules destruct the coupling of alcohols preventing the co-operative process of relaxation or due to the monomerisation of alcohols. These results indicate that a molecular association is taking place between alcohol molecules and alcohols with tetrahydrofuran. This association may arise due the hydrogen bond formation between the hydrogen atoms of alcohol with the oxygen atom of tetrahydrofuran [33, 34].

The result shows that thermodynamic parameters value lies below the corresponding values of the pure components. This indicates that the interaction between dissimilar molecules may lower the activated states. The individual characteristics of the liquids are retained in cyclohexnone [35].ΔS and ΔH also throw some light on molecular structure [36]. Value of $\Delta S\tau$ is positive for pure tetrahydrofuran, cyclohexanol. The positive value of ΔS is an indication for the non-cooperative motion with more disorderliness. It is also pointed out the different value of may refer to the different degree of disorderliness in different systems. $\Delta S\eta$ is negative the addition of tetrahydrofuran brings more disorderliness to the mixture. This confirms the presence of hetero interaction in the mixture leading to the breaking of associated alcohol molecules which may reduce the orderliness.the difference in the value of and is due to the fact that the process of breaking and making of H-bonds in the mixture takes place at different extents.

5. Conclusion:

Using the values of static dielectric constant and dielectric constantat optical frequency, dipolar increment values have been calculatedfor the studied systems. Dipole moment of the complex is obtainedfrom the plot of $\Omega_B$vs $C_A/C_B$is straight line. In the studied systems 1:1complex formation is identified. From the value of $\Delta\mu$, it is concluded that interaction between the molecules is due to polarization effect. The relaxation studies conforms the interaction between the molecules.

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