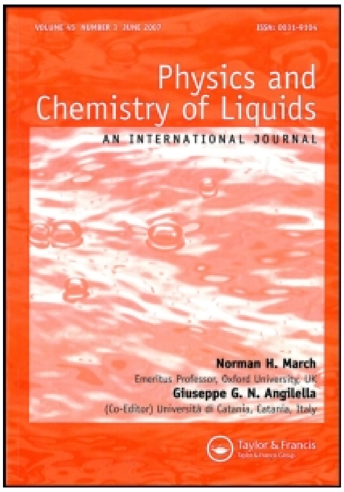

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Relaxation and thermodynamic studies of liquid mixtures of anisole with isopropanol in benzene

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Dielectric relaxation behaviour in polar–polar mixtures of anisole and isopropyl alcohol in benzene has been observed using the measurements of dielectric permittivity and dielectric loss at microwave frequency at three different temperatures. Using the Higasi method, average relaxation time, relaxation time for intra-molecular rotation and inter-molecular rotation have been calculated for the mixtures at different compositions. Viscosity and density of the mixtures are obtained over the entire range of concentration and temperature studied. Thermodynamic parameters, such as enthalpy and entropy, have been calculated for all studied concentrations, i.e. pure liquids and their mixtures. Activation free energies due to dielectric relaxation and viscous mechanisms for the system are discussed.

Keywords: relaxation time; viscosity; permittivity; molecular interaction

1. Introduction

Molecular interaction between the components in the liquid mixture has been identified by using the dielectric parameters such as the Kirkwood parameter, the Bruggeman parameter and excess parameters [1–3]. Molecular association between the molecules of a polar solute in a non-polar solvent has been studied using the microwave relaxation method [4,5]. In recent years, many researchers have studied the molecular association in the mixture of two polar components with or without dilution using microwave relaxation [6–8]. Using the permittivity values at microwave frequency (9.55 GHz), static frequency (1 KHz) and optical frequency, the dielectric relaxation time is calculated employing the Higasi and Cole methods. The Higasi method yields the relaxation time for intra-molecular rotation (τ_1) as well as inter-molecular rotation (τ_2), whereas the Cole method gives single relaxation time. The relaxation time only gives information about rotational motion, but a viscous study provides information on both rotational and translation motions [9]. Volumetric and viscometric investigations of liquid mixtures enable the determination of some useful thermodynamic and other parameters that are highly sensitive to

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molecular interactions [10]. In this investigation, we report the molecular dynamics of a mixture of anisole with isopropanol in benzene at different temperatures and concentrations. Anisole is a phenolic ether which contains a methyl group in its *para* position. Anisole is used in perfumery and as an insect pheromone. Isopropanol is mostly used as a cleaning agent and is often used for cleaning electronic devices such as contact pins, floppy disk drive heads and magnetic tap decks, which consist of the OH group. The investigation has been carried out due to the above-cited merits of the chemicals.

2. Material and methods

AR grade chemicals such as ansiosle, isopropanl and benzene were purchased from Sisco Research Laboratories Pvt. Ltd., Bombay, and were used without further purification. The mixture of anisole with isopropanol was prepared by adding them at different mole fractions and used as solute. The mole fraction of the solute in benzene was kept as 0.07. The permittivity (ε') and dielectric loss (ε'') at microwave frequency (9.82 GHz) were obtained using an X-band microwave bench [11]. Static permittivity (ε_0) of the samples was determined from the measured capacitance value of a cylindrical cell with and without the sample using a digital V-LCR capacitance metre supplied by M/S. Vasavi Electronics, Secunderabad, which was calibrated using some liquids of known static permittivity [12]. Abbe's refractometer was used for the measurement of refractive index corresponding to sodium D-line, the square of which was taken as permittivity at optical frequency (ε_∞). Density was obtained using a 10 mL R.D. bottle and a K-Roy balance. Viscosity of the sample was measured using Oswald's viscometer. The desired temperature of the solution was maintained by the circulation of water using a thermostat arrangement. The error in the measurement of capacitance, refractive index and temperature was ±0.1 pF, ±0.001 and ±0.1 K, respectively.

3. Theory

Conformational changes occurred when two or more liquids are mixed together, which can be studied by relaxation mechanisms.

3.1. *Higasi method*

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

$$\begin{aligned} \varepsilon_0 &= (\varepsilon_1 + a_0 w_2) \\ \varepsilon' &= (\varepsilon_1 + a'' w_2) \\ \varepsilon'' &= (a'' w_2) \\ \varepsilon_\infty &= (\varepsilon_{1\infty} + a_\infty w_2), \end{aligned} \tag{1}$$

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

Higasi [13] (see also [14]) derived a relation connecting τ_0 and α.

$$\begin{aligned}\tau_0 &= \frac{1}{\omega}\left(\frac{A^2+B^2}{C^2}\right)^{\frac{1}{2(1-\alpha)}}\\ (1-\alpha) &= \frac{2}{\pi}\tan^{-1}\left(\frac{A}{B}\right),\end{aligned} \tag{2}$$

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

$$\begin{aligned}A &= a''(a_0-a_\infty)\\ B &= (a_0-a')(a'-a_\infty)-a''^2\\ C &= (a'-a_\infty)^2+a''^2.\end{aligned}$$

The Debye equation in terms of a_0, a', a'' and a_∞ yields two independent equations [15]:

$$\tau_1 = \frac{a''}{\omega(a'-a_\infty)} \tag{3}$$

$$\tau_2 = \frac{a_0-a'}{\omega a''}. \tag{4}$$

3.2. *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 centre 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 following equation [16].

$$(\omega\tau)^{1-\alpha} = \left(\frac{v}{u}\right), \tag{5}$$

where α is the distribution parameter, ω is the angular frequency, v is the distance between ε_o and experimental point on the Cole–Cole plot, and u is the distance between ε_∞ and that point on the Cole–Cole plot.

Eyring relations are used to compute the activation free energy from the equations given below [17].

$$\tau = \left(\frac{h}{kT}\right)\exp\left(\frac{\Delta F_\tau}{RT}\right) \tag{6}$$

$$\eta = \left(\frac{Nh}{V}\right)\exp\left(\frac{\Delta F_\eta}{RT}\right), \tag{7}$$

where N, k, h, R, V and T are Avogadro's number, Boltzmann's constant, Planck's constant, gas constant, molar volume and temperature, respectively. ΔF_τ refers to the activation free energy due to the relaxation mechanism, and ΔF_η stands for activation energy due to viscosity.

4. Results and discussion

Static permittivity (ε_0), permittivity (ε') and dielectric loss (ε'') at microwave frequency, permittivity at optical frequency (ε_∞), density (ρ) and viscosity (η) for the mixture of anisole + isopropanol have been obtained as a function of temperature and concentration, and the values are reported in Table 1. The dielectric parameters given above are employed to calculate the relaxation time. At each temperature, values of ε_0, ε' and ε'' increase with increasing the concentration of the alcohols, whereas ε_∞, ρ and η decrease with the increasing concentration of the alcohol. This confirms the interaction between the molecules of the components in the mixture.

Though the value of α is small, it is finite. Hence, this confirms that anisole has a distribution of relaxation times. Garge and Smyth [18] have reported two relaxation times for anisole, one for overall relaxation and another for the methoxy group rotation. Formation of monomer and dimmer in anisole has been reported by Reimann *et al.* [19]. Two relaxation mechanisms for the mixture of anisole with fluorine have been reported by Farmer *et al.* [20]. Hence, it is more probable that anisole can have a distribution of relaxation times. We have observed two relaxation times for anisole and the mixture, one for the overall rotation of the molecule and another for the intra-molecular rotation. Our results are in agreement with the views reported by Reimann *et al.* The value of most probable relaxation time (τ_0) for the

Table 1. Variation of ε_0, ε', ε'', ε_∞, ρ, η values with concentration of isopropanol in anisole in benzene.

X_2	ε_0	ε'	ε''	ε_∞	ρ (g/cc^{-1})	η (Pascal)
Anisole + isopropanol in benzene at 303 K						
0.0	2.5042	2.4809	0.0560	2.2362	0.8749	0.000603
0.3	2.5266	2.4894	0.0553	2.2296	0.8688	0.000593
0.5	2.5426	2.4962	0.0621	2.2201	0.8622	0.000578
0.7	2.5674	2.5129	0.0681	2.2177	0.8636	0.000577
1.0	2.5906	2.5309	0.0755	2.2130	0.8577	0.000574
Anisole + isopropanol in benzene at 313 K						
0.0	2.4472	2.4316	0.0429	2.2267	0.8692	0.000529
0.3	2.4746	2.4435	0.0481	2.2183	0.8643	0.000526
0.5	2.4978	2.4581	0.0557	2.2135	0.8561	0.000510
0.7	2.5130	2.4680	0.0598	2.2118	0.8595	0.000508
1.0	2.5386	2.4841	0.0682	2.2028	0.8514	0.000505
Anisole + isopropanol in benzene at 323 K						
0.0	2.4002	2.3892	0.0334	2.2159	0.8655	0.000458
0.3	2.4386	2.4120	0.0436	2.2135	0.8598	0.000455
0.5	2.4610	2.4262	0.0513	2.2028	0.8516	0.000441
0.7	2.4738	2.4345	0.0548	2.1999	0.8509	0.000438
1.0	2.4930	2.4471	0.0611	2.1951	0.8475	0.000436

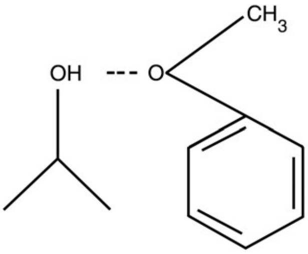

Figure 1. Hetero molecular interaction of anisole and isopropanol molecules.

mixtures is below the corresponding value of the components. This shows the presence of the hetero interaction between isopropanol and anisole, which is clearly presented in Figure 1. Vyas and Vahistra [21] have reported that the relaxation time for a polar liquid mixture is greater than the corresponding values of the components indicating the existence of solute–solute molecular association between the component molecules resulting in the formation of a heavier entity than the individual molecule. But in our investigation, τ_0 values of the mixture are below the corresponding values of the components. This may be taken that the interaction between the components is such as to form association between the component molecules, resulting in an entity whose size is smaller than the individual molecules. The value of the most probable relaxation time obtained by Cole–Cole and Higasi methods are found to have a close agreement. A small discrepancy in the value of the most probable relaxation time is obtained from the different methods. This trend exists at all the three temperatures. Sharma and Gandhi [22] have reported that a polar liquid mixture with both components as associative or non-associative has a single relaxation time, whereas if one of them is associative and the other one is non-associative, it has two relaxation times. However, our results are contradictory to the views reported by Shama *et al*. Though both anisole and isopropanol are associative, we get two relaxation times. The same trend is found to exist at all the three studied temperatures. Branin and Smyth [23] have reported that for a polar liquid mixture, if the value of τ_0 lies between the τ_0 values of the individual components then an overlap of two individual dispersion regions takes place. For the system studied, at all the three temperatures the τ_0 value does not lie in between the corresponding values of the components. This shows that the overlapping of the individual dispersion regions is not possible.

Perusal of Table 2 indicates that the value of τ_0 decreases with the increase in temperature. This may be explained on the basis of Debye's theory [24]. Similar views have been reported by Rewar and Bhatnagar [25], and they have pointed out that besides the change in molar volume, the rate of loss of energy number of collisions dominates, and hence molecules reorient at a faster rate when the field changes its direction. τ_0 values are found to increase with the increase in concentration of the alcohol. This shows the size of the clusters increase with the increase in concentration of the alcohol. The increase in τ_0 value may be due to the increase in size of the clusters or it may be due to the fact that less hindrance is offered due to viscous force. As viscosity of the mixture decreases with the increasing concentration of alcohol, it can be concluded that the increasing size of the molecule

Table 2. Variation of distribution parameters, relaxation times and excess relaxation time values with concentrations of isopropanol in anisole.

X_2	Higasi method			Cole–Cole method		
	τ_0 (ps)	τ_1 (ps)	τ_2 (ps)	α	β	τ (ps)
Anisole + isopropanol in benzene at 303 K						
0.0	4.1303	4.4223	6.7882	0.0820	0.1080	3.3209
0.3	3.3553	4.0696	10.9751	0.2209	0.2436	2.6279
0.5	3.5304	4.2570	12.1903	0.2456	0.2676	2.7907
0.7	3.5835	4.3215	13.0569	0.2645	0.2858	2.8529
1.0	3.6777	4.4024	13.5924	0.2740	0.2785	2.9980
Anisole + isopropanol in benzene at 313 K						
0.0	3.5721	3.8584	5.9328	0.0737	0.0901	3.0615
0.3	3.1620	3.8907	10.5489	0.2160	0.2306	2.6769
0.5	3.3692	4.1101	11.6286	0.2367	0.2514	2.2882
0.7	3.4438	4.1927	12.2773	0.2502	0.2638	2.9616
1.0	3.5769	4.3161	13.0377	0.2641	0.2786	3.0964
Anisole + isopropanol in benzene at 323 K						
0.0	3.0843	3.3742	5.3732	0.0722	0.0818	2.8135
0.3	3.1077	3.8100	9.9537	0.2023	0.2113	2.8207
0.5	3.2076	3.9554	11.0678	0.2277	0.2352	2.9540
0.7	3.2426	4.0129	11.7004	0.2422	0.2498	2.9886
1.0	3.3898	4.1501	12.2564	0.2512	0.2575	3.1443

may be responsible for the increasing relaxation times. This indicates that the size of the clusters is smaller in the mixture than in the individual liquids.

For all the solutes and their ternary mixtures, the values of τ_2 are significantly different from those of τ_0 and τ_1. This confirms the presence of both inter-molecular and intra-molecular relaxation processes. Similar results are reported by Rewar and Bhatnagar [25]. Moreover, $\tau_1 < \tau_2$ indicates that the contribution by inter-molecular relaxation is greater compared to intra-molecular relaxation. The finite value of the intra-molecular relaxation time (τ_1) in the mixture suggests the presence of intra-molecular motion of the molecules in the mixture. It is also noted that τ_1 does not vary much with viscosity, whereas τ_2 depends on viscosity. The activation free energy due to relaxation mechanism (ΔF_τ) and viscous force (ΔF_η) for different temperatures are reported in Table 3. The most probable relaxation time from the Higasi method is used to calculate the activation free energy entropy and enthalpy due to the relaxation mechanism. It is seen that at all concentrations and temperatures, ΔF_η values are greater than ΔF_τ values. This indicates that the relaxation mechanism involves only rotational motion, whereas viscous motion involves both rotational and translation motion [9]. The value of ΔF_τ for the three compositions of the mixture at any given temperature is less than the corresponding values for their pure components. Similar views have been reported by Sharma and Gandhi [22] for the mixture of acetates. The molar free energy of activation for the dielectric process decreases with an increase in temperature, as in the case of pure components. But molar free energy of activation for the process of viscous flow increases with an increase in temperature, as in pure states. This indicates that with a rise in temperature which results in the fall of viscosity of the surrounding medium,

Table 3. Activation energies of mixtures of anisole + isopropanol in benzene at studied concentrations and temperatures.

	ΔF_τ (Joule)			ΔF_η (Joule)		
X_2	303 K	313 K	323 K	303 K	313 K	323 K
0.0	8230	7863	7492	12,447	12,534	12,557
0.3	7705	7555	7512	12,391	12,501	12,523
0.5	7833	7715	7591	12,319	12,411	12,442
0.7	7871	7771	7619	12,298	12,389	12,403
1.0	7937	7866	7731	12,265	12,355	12,368

Table 4. Values of enthalpy and entropy for anisole + isopropanol in benzene at various concentrations.

X_2	ΔH_τ (Joule)	ΔS_τ (Joule)	ΔH_η (Joule)	ΔS_η (Joule)
0.0	311.14	3.53	4873.24	−1.79
0.3	540.69	−23.60	4688.37	−2.32
0.5	1296.08	−21.57	4799.69	−1.86
0.7	1471.01	−21.16	4880.20	−1.56
1.0	707.67	−23.90	4875.23	−1.53

and a rise in thermal agitation, the molecules of the system as a whole require more energy to come to the activated states. The molar enthalpy of activation (ΔH) and the molar entropy of activation (ΔS) for the dielectric relaxation process and viscous flow process are given in Table 4, which can also give information on molecular structure. The value of ΔS_τ for anisole is positive, whereas ΔS_τ for isopropanol and the mixtures is negative. According to Branin *et al.* [23] a negative entropy of activation indicates that there are few configurations; the activated state is more ordered than the normal state. The presence of cooperative orientation of the molecules from steric force or a parallel alignment of the dipoles involved in dipole–dipole interaction may be the reason for this behaviour. Our system also shows similar behaviour. The value of ΔH for the mixtures is positive. The positive value of ΔH suggests that the reaction is endoergic and heat is absorbed. The energy is absorbed due to the formation of H-bonds. This result is the conversion of monomers into multimers, increasing the orderliness, leading to co-operative orientation. Sharma and Sharma [26] have pointed out that the difference in the value of ΔH_τ and ΔH_η is due to the fact that the process of breaking and making of bonds in the mixture is taking place to different extents. In the system studied, the fact that the values of ΔH_τ and ΔH_η are different from each other agrees with the reports of Sharma *et al.*

5. Conclusion

Dielectric relaxation measurements have been carried out on the mixture of anisole + isopropanol in benzene at three different temperatures. Density and viscosity measurements were also taken for the studied system. Higasi and Cole methods were employed in the calculation of relaxation time. The activation free energy due to relaxation and viscous mechanisms has been obtained, and the proper interpretations given. Eyring's rate process is found to be applicable for the studied system.

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