Study of dielectric relaxation and dipole moment of some binary mixtures using microwave absorption data

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Abstract

The dipole moment and dielectric relaxation time of different concentration binary mixtures of 1-propanol and alkyl benzoates (Methyl Benzoate and Ethyl Benzoate) have been measured at microwave frequency 9.132 GHz at different temperatures. Thermo dynamical parameters like molar free energy of activation (ΔF_ε), molar enthalpy of activation (ΔH_ε) and molar entropy of activation (ΔS_ε) have been evaluated by considering the relaxation as the rate process.

Key words: Dielectric relaxation, Relaxation time, Dipole moment, hydrogen-bonding, molar free energy of activation, molar enthalpy of activation.

1. Introduction

The dielectric relaxation study of solute solvent mixture at microwave frequency gives information about molecular interactions in the system, formation of monomers and multimers. Dielectric relaxation spectroscopy was proved to be a powerful tool for the investigation of hydrogen bond rearrangement dynamics and has been widely applied to study the pure solvents and solute- solvent mixtures[1-2]. Many workers have reported dielectric relaxation studies of polar molecules and their binary mixtures in dilute solutions of non-polar solvents[3–7] as well as in pure state[8–12].

Dielectric investigation of binary polar liquid mixtures consisting of one associative and other non-associative liquid provides valuable information regarding molecular complex formation in solution. Alcohols are industrially and scientifically important organic compounds and their physical and chemical properties are largely determined by the – OH group. Alcohols are strongly associated in solution because of dipole-dipole interaction and hydrogen bonding. Alkyl benzoates are non-associated in solution, good hydrogen bonding acceptors and important industrial chemicals that are widely used in perfumery and pesticides. The strength of the molecular association depends on several factors including the molecular

structure, temperature, solvent and other factors[13]. The presence of hydrogen bond brings a considerable change in the dielectric properties of liquid mixtures. Therefore, the solution chemistry of these compounds can be strongly influenced by the aggregation phenomena, which can play a significant role in physical properties like refractive index, dielectric permittivity, density and molar volume[14-16].

In the course of present study, to get better understanding of the nature of molecular orientation process, we studied the temperature dependent dielectric relaxation in pure and binary mixtures of propanol-1(1PN) with methyl benzoate (MB) and ethyl benzoate (EB).

2. Experimental Details

The compounds propan-1-ol (1PN), methyl benzoate (MB) and ethyl benzoate (EB) of AR grade were obtained from Central Drug House, New Delhi and are purified using standard methods. The binary mixtures are prepared for different mole fractions. The X-band microwave bench was used to measure wavelength in the dielectric medium and voltage standing wave ratio (VSWR) using a short-circuiting plunger. All the measurements were carried out at 295, 305, 315 and 325 K by circulating water around the dielectric cell through a thermostat (Mittal Enterpises, New Delhi, India). Densities at different temperatures are measured by using a 10 ml specific gravity bottle and an electronic balance whose accuracy is 0.01 mg. The high frequency dielectric permittivity ($\varepsilon_\infty = n^2$) is obtained using Abbe refractometer with sodium D light as source at different temperatures.

3. Theory :

The dielectric constant (ε') and dielectric loss (ε'') have been calculated by the method of Heston $et\ al.$[17] using the following relations:

$$\varepsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \tag{1}$$

And

$$\varepsilon'' = \left(\frac{2\lambda_0^2}{\pi\lambda_d\lambda_g}\right)\left(\frac{d\rho}{dn}\right) \tag{2}$$

Where $\lambda_0,\ \lambda_c, \lambda_g$, and λ_d are the free space wavelength, the cut-off wavelength, the waveguide wavelength and the wavelength in the waveguide filled with solution, respectively. ρ is the inverse of voltage standing wave ratio (VSWR) and $(d\rho/dn)$ is the slope of ρ versus n curve, where n = (1, 2, 3…….) such that (n $\lambda_d/2$) represents the length of dielectric filled waveguide. The ε' and ε'' values from repeated measurements were reproducible within ±0.05 and ± 1.67, respectively.

The dielectric relaxation time (τ) and dipole moment (μ) have been calculated by using the Gopala Krishna's[18] single frequency concentration variation method

$$X = \frac{\varepsilon'^2 + \varepsilon' + \varepsilon''^2 - 2}{\left(\varepsilon' + 2\right)^2 + \varepsilon''^2} \tag{3}$$

$$Y = \frac{3\varepsilon''}{\left(\varepsilon' + 2\right)^2 + \varepsilon''^2} \tag{4}$$

$$\mu^2 = \frac{9kTM}{4\pi Nd_0}\left[1 + \left(\frac{dY}{dX}\right)^2\right]\frac{dX}{dW} \tag{5}$$

$$\tau = \frac{\lambda_0}{2\pi c}\left(dY\big/dX\right) \qquad (6)$$

The energy parameters (ΔH_ε, ΔF_ε, and ΔS_ε) for dielectric relaxation process for alkyl benzoates and 1PN mixture containing 50 mol% alkyl benzoates in 1PN at different temperatures have been calculated by using Eyring et al.[19], relations for the rate process. Following relations were used:

$$\tau = \frac{h}{kT}\exp\left(\Delta F_\varepsilon\big/RT\right) \qquad (7)$$

$$\Delta F_\varepsilon = \Delta H_\varepsilon - T\Delta S_\varepsilon \qquad (8)$$

Where ΔH_ε, ΔF_ε, and ΔS_ε are the enthalpy, free energy and entropy of activation, respectively for dielectric relaxation process and all other symbols have their usual meaning. ΔH_ε has been determined by slope of the plot of $\ln(T\tau)$ versus $1/T$, while ΔF_ε, and ΔS_ε are calculated using Eqs (7) and (8) respectively.

4. Results and Discussion

Table 1 and Table 2 report the values of the dielectric relaxation time with mole fraction of alkyl benzoates (MB and EB) in 1PN mixture at different temperatures. The relaxation time(τ) of pure 1PN are higher and is due to the formation of intra molecular hydrogen bonding between one alcohol molecule and another (R-O-H…OH-R), which leads to the formation of self associated groups. The increase in the number of self associated groups cause to absorb more electromagnetic energy. Due to this, molecules relax very slowly leading to higher relaxation times. But the relaxation time of pure MB and

EB are very low as compared to pure 1PN. The relaxation times of pure EB are greater than of pure MB due to the increase in molecular size and effective radius of the rotating unit. The relaxation times are found to decrease as the concentration of MB and EB increases in 1PN at all temperatures as shown in Figs 1 and 2, respectively. Similar trend in relaxation time values has already observed using LF impedance analyzer by T Madhu Mohan[7].

At high concentrations of alcohol in the mixture, there are large number of 1PN molecules surrounding the benzoate molecule and these associative alcohol molecules are forming hydrogen bond with the benzoate molecules. At low concentration of 1PN in the mixtures, there are only a small number of alcohol molecules to enable dipole-dipole interaction through hydrogen bonding with the non-associative benzoate molecules. As a result, weak intermolecular interaction occurs. The relaxation time increases with increasing alkyl chain length of benzoate indicating that the degree of co-operation for reorientation of the molecules increases with increasing length and the bulk of cluster increases. So the formation of hydrogen bonding between hydroxyl group (-OH) of 1PN and –CH group of benzoates restricts the free internal rotation of the molecules.

The value of the dipole moment for alkyl benzoates in 1PN are reported in Table 3 and 4. The value of the dipole moment of 1PN (binary mixture with 0.00 mole fraction) (Table 3) is found to change slightly with temperature. The slightly temperature dependent variation of dipole moment of the rotating molecular entity may predict the solute-solvent
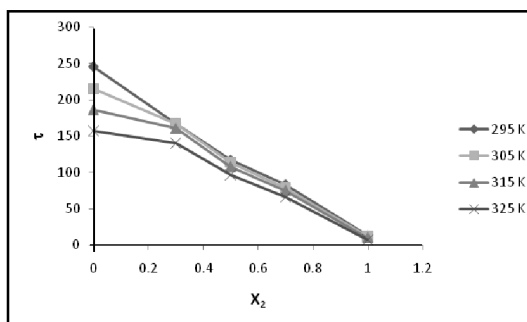
Fig. 1. Relaxation time (τ) with mole fraction (X) of MB in 1-PN at different temperatures
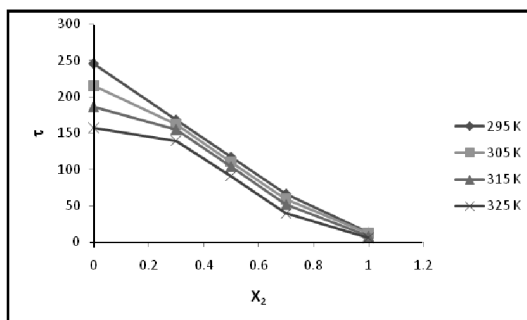

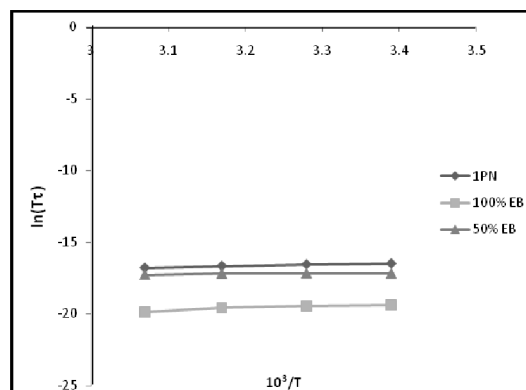Fig. 2. Relaxation time (t) with mole fraction (X_2) of EB in 1-PN at different temperatures

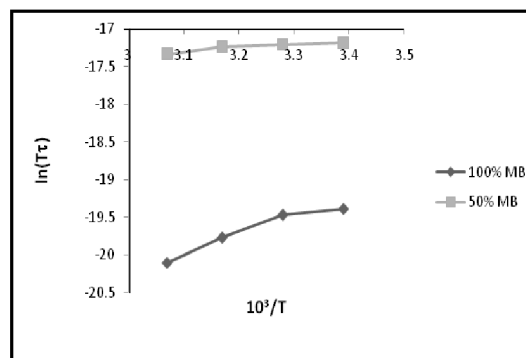Fig. 3. Plots of $\ln(T\tau)$ versus 1/T for pure 1PN, pure EB and 50% EB in 1PN

Fig. 4. Plots of $\ln(T\tau)$ versus 1/T for pure MB and 50% MB in 1PN

Table 1. Values of dielectric relaxation time (τ) with mole fraction (X_2) of Methyl benzoate in Propan-1-ol at different temperatures

Mole Fraction	Dielectric Relaxation Time(τ) in ps			
	295K	305K	315K	325K
0.00	245.42	215.85	186.08	157.79
0.30	167.31	166.89	160.43	140.54
0.50	116.99	114.25	107.91	96.82
0.70	83.22	79.18	74.99	66.25
1.00	12.96	11.78	10.22	7.13

Table 2. Values of dielectric relaxation time (τ) with mole fraction (X_2) of Ethyl benzoate in Propan-1-ol at different temperatures

Mole Fraction	Dielectric Relaxation Time(τ) in ps			
	295K	305K	315K	325K
0.00	245.42	215.85	186.08	157.79
0.30	167.89	162.15	154.75	139.92
0.50	116.76	110.48	103.91	91.31
0.70	65.93	58.95	51.39	39.23
1.00	12.79	11.46	8.23	5.71

Table 3. Values of dielectric relaxation time (τ) and dipole moment (μ) for different mole fractions (X_2) of (Ethyl benzoate + Propan-1-ol) mixtures at different temperatures

Temperature(K)	Mole fraction	τ(ps)	μ(D)
295	0.00	245.42	1.53_{1PN}
	0.30	167.89	
	0.50	116.76	
	0.70	65.93	
	1.00	12.79	2.94_{EB}
305	0.00	215.85	1.56_{1PN}
	0.30	162.15	
	0.50	110.48	
	0.70	58.95	
	1.00	11.46	2.96_{EB}
315	0.00	186.08	1.58_{1PN}
	0.30	154.75	
	0.50	103.91	
	0.70	51.39	
	1.00	8.23	2.99_{EB}
325	0.00	157.79	1.61_{1PN}
	0.30	139.92	
	0.50	91.31	
	0.70	39.23	
	1.00	5.71	3.31_{EB}

Table 4. Values of dielectric relaxation time (τ) and dipole moment (μ) for
different mole fractions (X_2) of (Methyl benzoate + Propan-1-ol)
mixtures at different temperatures

Temperature(K)	Mole fraction	τ(ps)	μ(D)
295	0.00	245.42	1.53_{1PN}
	0.30	167.31	
	0.50	116.99	
	0.70	83.22	
	1.00	12.96	1.78_{MB}
305	0.00	215.85	1.56_{1PN}
	0.30	166.89	
	0.50	114.25	
	0.70	79.18	
	1.00	11.78	1.81_{MB}
315	0.00	186.08	1.58_{1PN}
	0.30	160.43	
	0.50	107.91	
	0.70	74.99	
	1.00	10.22	1.85_{MB}
325	0.00	157.79	1.61_{1PN}
	0.30	140.54	
	0.50	96.82	
	0.70	66.25	
	1.00	7.13	1.87_{MB}

type of molecular association. MB and EB shows the similar behavior.

The plot of $\ln(T\tau)$ versus $1/T$ has been shown in Fig. 3 and 4. The molar enthalpy of activation and molar entropy of activation for individual polar components and their equi molar mixtures are reported in Table 5. It is evident from Table 5 that free energy of activation (ΔF_ε) is not same for all molecules, which indicates that force of hindrance experienced by molecules for dipole rotation is

a factor dependent on the nature of molecules. In the present study it is found that ΔF_ε values increase with temperature. Increased temperature decreases viscosity of solvent but increases thermal agitation, so that molecules of the system require more energy to overcome the excited state. The values of molar entropy of activation (ΔS_ε) for the relaxation processes of pure 1PN and the equimolar mixture of alkyl benzoates (MB and EB) in 1PN is negative. But for pure MB and pure EB ΔS_ε values are positive. Negative ΔS_ε values indicate that

Table 5. Thermo dynamical parameters of pure alkyl benzoates and their
binary mixtures at different temperatures

Name of the sample	Temperature K	ΔH_ε(kJ mol^{-1})	ΔF_ε (kJ mol^{-1})	ΔS_ε(kJ mol^{-1}K^{-1})
Methyl benzoate	295	43.25	16.134	0.0919
	305		16.704	0.0870
	315		17.188	0.0827
	325		17.526	0.0791
Ethyl benzoate	295	28.57	16.129	0.0421
	305		16.620	0.0392
	315		17.089	0.0364
	325		17.367	0.0344
Propan-1-ol	295	18.78	36.941	-0.0615
	305		37.952	-0.0628
	315		38.893	-0.0638
	325		39.765	-0.0645
50% mol MB in 1PN	295	8.44	35.124	-0.0904
	305		36.399	-0.0916
	315		37.465	-0.0921
	325		38.446	-0.0923
50% mol EB in 1PN	295	5.30	35.119	-0.1010
	305		36.254	-0.1014
	315		37.366	-0.1017
	325		38.285	-0.1014

activated state is more ordered in comparison to normal state as dipoles are more aligned in the activated state. Negative ΔS_ε values also indicate existence of cooperative orientation. Positive values of ΔS_ε suggest that cooperative orientation in the single component system becomes non-cooperative in mixture system, which resulting in the activated state, which is more disordered in comparison to normal state. The small values of ΔS_ε for the mixtures indicate that intra-molecular mechanisms make a large contribution to the dielectric absorption.

5. Conclusion

The dielectric relaxation time, dipole moment, molar free energy of activation, molar enthalpy of activation and molar entropy of activation are computed for the pure and binary mixture system of propan-1-ol and ethyl benzoate and methyl benzoate at different temperatures for various mole fractions. The formation of hydrogen bond between the mixture systems is identified by studying the variation in the parameters determined.

Acknowledgement

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