

Dielectric Relaxation Studies of Ternary Mixtures of N- Butyl Iodide with Isovaleric Acid in Benzene in the Microwave Region

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ABSTRACT: The values of the static dielectric constant (ϵ_0), dielectric constant at optical frequency (ϵ_∞), dielectric constant (ϵ'), the dielectric loss (ϵ'') at microwave frequency for different molar ratios at different temperatures for ternary system have been measured. Based on the values dielectric relaxation time τ_0, τ_1, τ_2 and distribution parameter α have been calculated by both Higasi and Cole-Cole method

KEYWORDS: Dielectric relaxation, Dielectric constant, Optical frequency, Higasi Method, Cole -Cole method, N- Butyl Iodide, Isovaleric Acid.

I INTRODUCTION

Many researchers [1-8] studied the association of two polar molecules due to hydrogen bonding from the dielectric relaxation measurements at microwave frequencies. The importance of measuring the static permittivity constant of liquid lies in the fact that it provides valuable information about ordering of the molecules in the liquid state. The study also gives information about the molecular interaction in binary mixture.

II MATERIALS AND METHODS

N-Butyl iodide with isovaleric acid in benzene was used. The molar fraction of the n-Butyl iodide with isovaleric acid in benzene are 0,0.33,0.5,0.67 and 1.0. The static dielectric constant ϵ_0 measured by frequency technic at three different temperatures. The refractive index was measured by Abbe's refractometer. Using microwave frequency (9.4974E+09 MHz), the dielectric constant at an angular frequency ϵ' and dielectric loss ϵ'' was measured. The errors in measurements of refractive index (n_D) and density are ± 0.002 and ± 0.002 g/cc respectively. Using Temperature controlled water circulating thermostat 0.1°C accuracy maintained for 303K, 308K and 313K.

III THEORY

Higasi Method

The dielectric relaxation time (τ) was calculated using Higasi's method [9-12].

Assuming $\epsilon_0, \epsilon', \epsilon''$, And ϵ_∞ vary linearly with weight fraction w_2 of the Solute. We have:

$$\epsilon_0 = \epsilon_1 + w_2 a_0 \quad (1)$$

$$\epsilon' = \epsilon_1 + w_2 a' \quad (2)$$

$$\epsilon'' = a'' w_2; \epsilon_\infty = \epsilon_{1\infty} + a_\infty w_2 \quad (3)$$

$$\epsilon_\infty = \epsilon_{1\infty} + a_\infty w_2 \quad (4)$$

The following expression were used for obtaining ϵ' and ϵ''

$$\epsilon' = \left[\frac{\lambda_0}{\lambda_c} \right]^2 + \left[\frac{\lambda_0}{\lambda_d} \right]^2 \quad (5)$$

$$\epsilon'' = \frac{2}{\pi} \left[\frac{\lambda_0 \lambda_0^4}{\lambda_d^3} \right] \left[\frac{dn}{dn} \right] \quad (6)$$

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

Where λ_d is the wavelength in the dielectric medium, λ_g the wave guide wavelength, λ_0 the free space wavelength, λ_c the cut off wavelength and $1/\rho$ is the standing wave ratio obtained by using a short circuited movable plunger.

The uncertainties in the measurement of ϵ' and ϵ'' are 1% and 5% respectively.

The relaxation time for various solutions was also obtained in term of two Debye relaxation mechanisms with the help of the following Equations for dilute solution of weight fraction w_2

$$\tau_1 = \frac{a''}{\omega[a' - a_{\infty}]} \quad (7)$$

$$\tau_2 = \frac{a_0 - a'}{\omega a''} \quad (8)$$

$$\tau_0 = \frac{1}{\omega} \left[\frac{A^2 + B^2}{C^2} \right]^{\frac{1}{2(1-\alpha)}} \quad (9)$$

Where

$$A = a''(a_0 - a_{\infty})$$

$$B = (a_0 - a')(a' - a_{\infty}) - a''^2$$

$$C = (a' - a_{\infty})^2 + a''^2$$

Where τ_1 is a sort of intramolecular relaxation time, τ_2 is dielectric relaxation time for overall rotation of the whole molecule, τ_0 is the most probable relaxation time, ω is the angular frequency, τ_1 and τ_2 depending on both the weight factor of such mechanism at a given concentration and temperature.

The free energy of activation of dielectric relaxation and viscous ΔF_r flow ΔF_η . Dipolar and viscous forces have been calculated using Eyring's Equation

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta F_r}{RT}\right) \quad (10)$$

$$\eta = \frac{Nh}{V} \exp\left(\frac{\Delta F_\eta}{RT}\right) \quad (11)$$

Where h is the Planck's constant, k is the Boltzmann constant, N is the Avogadro number and V is the molar volume R is the gas constant

Cole-Cole method

The measured values of ϵ_0 , ϵ' , ϵ'' and ϵ_∞ are fitted in a complex plane plot with a depressed circular arc. The angle made by the diameter d drawn through the center from the ϵ_∞ point and the abscissa axis is equal to $\alpha\pi/2$. From the Cole-Cole arc, the relaxation time τ can be found using the equation

$$(\omega\tau)^{(1-\alpha)} = v/u \quad (12)$$

The distribution parameter α

$$\alpha = 1 - \frac{2}{\pi} \tan^{-1} \left(\frac{a''(a_0 - a_{\infty})}{(a_0 - a')(a' - a_{\infty})} \right) \quad (13)$$

The presence of more than one relaxation time is indicated by the non-zero value of the distribution parameter α .

IV. RESULTS AND DISCUSSIONS

The static dielectric constant ϵ_0 of 1:1 is greater than other molar ratios. The static dielectric constant ϵ_0 , The dielectric constant at optical frequency ϵ_∞ and the distribution parameter α of the pure and mixtures decreases with increase of temperature. ϵ' and ϵ'' of the mixtures lies between the value of pure samples at all temperatures

For all the studied systems at all the three different temperatures value of ' α ', which is calculated by Higasi/Cole-Cole method, has the greater value at the equimolar concentration (1:1). This may be due to the fact, that the high temperature, the molecular rotations of solute molecules becomes faster and uniform in the solution. Our results agree with Krishnan et al [13], and many researchers [14-17],

The most probable relaxation time (τ_0) value for the mixtures is greater than the corresponding value of the pure liquids. This implies the enhancement of the cluster size. Mixing of two liquids, results in the formation of bigger molecular size which enhances the relaxation time (τ_0). The hetero linear interaction between acid and halide molecules is such as to form linear

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

multimer. In all the studied at temperatures, the value of τ_0 for the mixtures is greater than the value of pure liquids in benzene. This shows the existence of strong hetero interaction through H-bonding between dissimilar molecules.

Table 1 Values of ϵ_{0m} , $\epsilon_{\infty m}$, ϵ' , ϵ'' , ρ , α , τ_0 , τ_1 and τ_2 at different mole fractions (X_2) of N- BUTYL IODIDE & ISOVALERIC ACID (X_2) in BENZENE (X_1) HIGASI METHOD and COLE-COLE METHOD

TEMP (K)	Mole fractions (X_2)	ϵ_{0m}	$\epsilon_{\infty m}$	ϵ'	ϵ''	Relaxation Time (pico second)				Distribution Parameter		Activation Energy(kJ/moi)		
						Higasi's Method				Cole-Cole plot	Higasi	Cole - Cole	Higasi	Cole-Cole
						τ_0	τ_1	τ_2	τ					
303	0	2.5735	2.0812	2.4528	0.1560	9.43	7.32	12.97	9.74	7.12	0.16	0.17	11.12	10.41
	0.33	2.6668	2.0850	2.3761	0.2088	17.19	12.63	23.35	17.17	16.75	0.19	0.21	12.60	11.84
	0.50	2.9770	2.0855	2.3757	0.2294	24.84	13.93	43.94	24.74	38.90	0.33	0.34	14.20	12.77
	0.67	2.7929	2.0867	2.3695	0.2098	21.17	13.09	33.83	21.04	25.53	0.28	0.30	13.54	12.36
	1	2.4735	2.0492	2.2974	0.1729	14.45	12.38	17.07	14.54	13.31	0.10	0.12	11.81	11.42
308	0	2.5620	2.0613	2.4536	0.1625	8.67	7.20	11.18	8.97	6.91	0.12	0.12	10.97	10.42
	0.33	2.6428	2.0741	2.3822	0.2092	15.73	11.92	20.88	15.78	14.67	0.18	0.19	12.57	11.86
	0.50	2.9600	2.0825	2.3728	0.2287	24.55	13.88	43.04	24.44	37.57	0.32	0.34	14.42	12.99
	0.67	2.7625	2.0856	2.3688	0.2069	20.39	12.89	31.89	20.27	23.42	0.27	0.29	13.65	12.51
	1	2.4600	2.0420	2.2961	0.1701	13.75	11.89	16.15	13.86	12.54	0.10	0.11	11.91	11.53
313	0	2.5515	2.0542	2.4590	0.1656	7.92	7.10	9.36	8.15	6.78	0.07	0.08	10.72	10.38
	0.33	2.5961	2.0589	2.3858	0.2099	13.62	11.25	16.80	13.74	12.29	0.12	0.14	12.25	11.74
	0.50	2.9265	2.0783	2.3673	0.2292	24.07	13.97	40.91	23.91	34.86	0.31	0.33	14.57	13.18
	0.67	2.7390	2.0843	2.3651	0.2009	19.95	12.62	31.21	19.85	22.43	0.27	0.29	13.86	12.70
	1	2.4465	2.0349	2.2934	0.1692	13.15	11.60	15.17	13.26	11.97	0.08	0.10	11.98	11.65

The value of τ_1 varies with the concentration of the acid and it has its maximum value at equimolar concentration. Values of τ_1 decreases with rise of temperature. This may be due to the hindrance offered due to the thermal agitations. Beyond equimolar concentration self-association among like molecules may lead to the reduction in size which may be the reason for the decrease of τ_2 values.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

Value of τ_2 also decreases with increasing temperature. This implies that in addition with the viscous force, size of the cluster also plays a role in relaxation time. The decrease of relaxation time with rise of temperature may be explained on the basis of Debye's theory of dielectric relaxation [18]. It has been reported that increase of temperature decreases the potential barrier hindering the dipole orientations. Decrease of relaxation time with increasing of temperature has been reported by T.Kalaivani et al [19] and many authors [20-22].

This is expected since the viscous flow involves both rotation and translation motion encountering greater resistance from the neighbors. But in the case of $\Delta F\tau$, it involves only rotational motion and hence it needs lesser energy for its activation from one state into another. Results on similar lines have been reported by many workers [19, 23-25].

V. CONCLUSION

The hetero interaction between the samples has been analysed through the process of dielectric relaxation. The results are further confirmed by Cole-Cole method

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