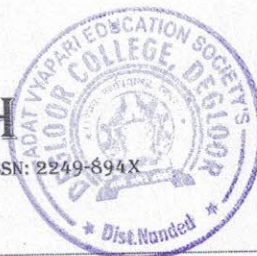




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DIELECTRIC RELAXATION AND THERMODYNAMIC PARAMETERS OF N-BUTYL ALCOHOL, ETHYLENEDIAMINE AND THEIR BINARY MIXTURES IN 1,4-DIOXAN.

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ABSTRACT :

The values of dielectric constant (ϵ') and dielectric loss (ϵ'') have been calculated for *n*-butyl alcohol, ethylenediamine and their binary mixtures in 1,4-dioxane at different temperatures using X-band microwave bench. The relaxation time (τ) and dipole moment (μ) have been calculated by employing Gopala Krishna's method. Thermodynamic parameters also have been calculated for dielectric relaxation as well as for viscous flow process. Observed values of Debye's factor and Kalman's factor shows that Kalman's formula satisfactorily explains the relationship between dielectric relaxation time and the viscosity. The non-linear behaviour of relaxation time with mole fraction reveals the presence of solute - solute molecular association in the mixture.

KEYWORDS : Dielectric relaxation, relaxation time, energy parameters, solute-solute association .

"INTRODUCTION"

Dielectric relaxation data obtained from the microwave absorption studies are expected to throw light on various types of molecular associations present in the solution. Dielectric relaxation studies of polar molecules in non-polar solvent from microwave absorption have been frequently attempted by number of research workers.¹⁻⁷ In the present paper, the dielectric relaxation study of *n*-butyl alcohol (*nBA*), ethylenediamine (*EDA*) and their binary mixtures in 1,4 dioxan were carried out for different mole fraction of *EDA* at different temperature. The study is expected to provide better understanding of the nature of molecular association in the mixture.

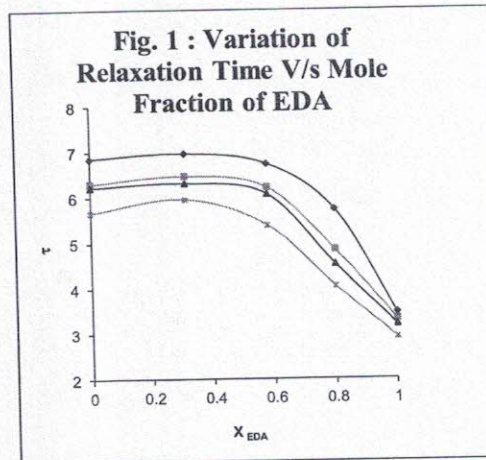
EXPERIMENTAL DETAILS:

n-butyl alcohol (*nBA*), ethylenediamine (*EDA*) and 1,4-dioxan all AR grade were procured from S.D. fine Chemicals, Mumbai and used without further purification. The liquids were mixed according to their proportion by volume. The X-band microwave bench² was used to measure voltage standing wave ratio (*VSWR*) and wavelength in dielectrics (λ_d) at temperatures 293, 303, 313 & 323°K. The dielectric constant (ϵ') and dielectric loss (ϵ'') were computed from these measurement. The dielectric relaxation time (τ) and dipole moment (μ) were calculated using Gopala Krishna's⁸ method. The free energy of activation ($\Delta F_\tau, \Delta F_\eta$), enthalpy of activation ($\Delta H_\tau, \Delta H_\eta$) and entropy of activation ($\Delta S_\tau, \Delta S_\eta$) for dielectric relaxation process and viscous flow process have been estimated using Eyring's equation⁹. The values of Debye factor (*C*) and Kalman's factor (*C'*) calculated using equations¹⁰ Values of dipole moment (μ) have been compared with values calculated by using relation

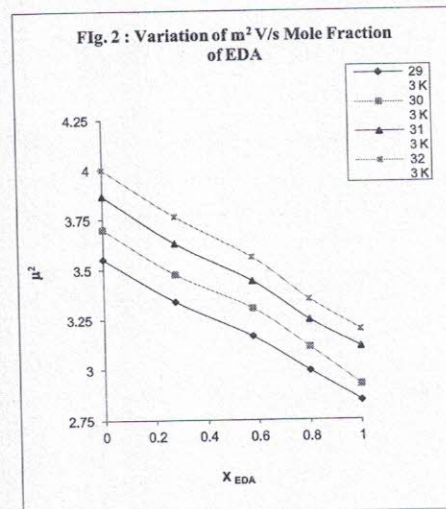
$$\mu^2 = X_1\mu_1^2 + X_2\mu_2^2 \quad (1)$$

where X_1 and X_2 are the mole fractions of two constituents in the mixture.

RESULT AND DISCUSSION.

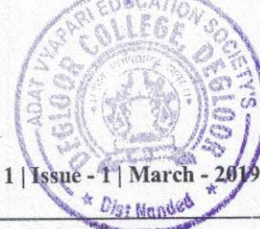


Values of dielectric parameters (ϵ' , ϵ'') and relaxation time (τ) for pure liquids and their mixtures are presented in table 1. The values of relaxation time are observed to decrease systematically with increase in temperature from 20°C to 50°C. This may be due to increase in temperature, which causes change in



molar volume and rate of loss of energy due to large number of collisions. Hence molecules reorient with faster rate. Similar kind of results presented by Rewar and Bhatnagar.¹⁸ Fig. 1 shows the variation of relaxation time with increasing mole fraction of *EDA*. The non-linear variation of relaxation time with mole fraction of one of the constituents is interpreted as possible solute – solute molecular association in the binary mixture. The molecular entities becomes much more voluminous than the individual molecules due to this association.

The values of Debye factor (C), Kalman's factor (C') and dipole moment (μ) are reported in the table 2. The dipole moment values are found to be increase with increase in temperature. This may be due to increase of dipole length for higher temperature. The variation of dipole moment with temperature may be attributed to solute – solvent association¹⁹. Fig. 2 shows variation of dipole moment with mole fraction of



EDA. This non-linear variation of (μ) suggest the solute - solute molecular association²⁰. The survey of table 2 shows that Debye factor (C) varies with temperature where as Kalman's factor (C') remains almost constant with temperature. This shows that Kalman's equation for dielectric relaxation time (τ) as a function of viscosity is superior to the Debye equation and the quantity η^x is a better representation of inner friction coefficient for dipolar rotation. Similar results were observed earlier by Khatri and Gandhi²¹, Khameshara and Sisodia²² and Singh and Sharma¹⁰.

The energy parameters for dielectric relaxation process and viscous flow process are presented in table 3. The free energy of activation (ΔF_τ) for dielectric relaxation process is found to be increases with increases in temperature. This may be due to with increase in temperature, the thermal agitation increases and dipole require more energy to be activate. It is found that the free energy of activation (ΔF_τ) for dielectric relaxation process is less than free energy of activation (ΔF_η) for viscous flow process. This is because of the dielectric relaxation process involves rotation of molecules only whereas in viscous flow process, the rotation as well as translational motion of the molecules is involved²⁰.

The enthalpy of activation (ΔH_η) for viscous flow process is found to be greater than the enthalpy of activation (ΔH_τ) for dielectric relaxation process and their ratio is found to be $\frac{\Delta H_\tau}{\Delta H_\eta} < 0.5$, suggesting the solid rotator phase²³. The entropy of activation (ΔS_τ) for dielectric relaxation process is found to be negative, suggesting activated state is more ordered than the normal state²⁴. In activated state the dipoles are more aligned than in normal state.

Table 1. The values of dielectric constant (ϵ'), dielectric loss (ϵ'') and relaxation time (τ) for different weight fraction of solute of n-butyl alcohol, ethylenediamine and their binary mixtures in 1,4-dioxan at different temperatures.

Temperature →		293°K			303°K			313°K			323°K		
Solute %	Wt. Fraction	ϵ'	ϵ''	τ ps	ϵ'	ϵ''	τ ps	ϵ'	ϵ''	τ ps	ϵ'	ϵ''	τ ps
nBA 100%	0.03745	2.677	0.203	6.85	2.638	0.183	6.30	2.602	0.168	6.22	2.583	0.134	5.66
	0.07220	2.767	0.269		2.730	0.243		2.710	0.216		2.692	0.203	
	0.10450	3.048	0.399		2.975	0.364		2.952	0.328		2.907	0.293	
	0.13470	3.159	0.484		3.087	0.441		3.063	0.407		3.018	0.364	
nBA (69%) + EDA (31%)	0.03882	2.692	0.214	6.96	2.655	0.192	6.47	2.634	0.171	6.31	2.620	0.152	5.95
	0.07474	2.855	0.313		2.845	0.283		2.807	0.288		2.767	0.237	
	0.10810	3.109	0.435		3.034	0.392		3.018	0.371		2.990	0.340	
	0.13910	3.209	0.525		3.183	0.484		3.136	0.455		3.109	0.422	
nBA (42%) + EDA (58%)	0.03472	2.806	0.269	6.73	2.786	0.233	6.22	2.767	0.213	6.07	2.728	0.185	5.38
	0.07641	2.931	0.345		2.908	0.316		2.846	0.280		2.814	0.261	
	0.11040	3.153	0.453		3.136	0.428		3.109	0.392		3.064	0.355	
	0.14200	3.312	0.505		3.234	0.499		3.183	0.481		3.110	0.442	
nBA (20%) + EDA (80%)	0.04060	2.767	0.234	5.73	2.748	0.287	4.85	2.730	0.202	4.53	2.692	0.237	4.04
	0.07804	3.064	0.407		3.018	0.368		2.996	0.338		2.972	0.296	
	0.11270	3.230	0.466		3.200	0.423		3.158	0.381		3.112	0.340	
	0.14480	3.478	0.598		3.450	0.558		3.393	0.492		3.337	0.441	
EDA (100%)	0.04168	2.767	0.271	3.46	2.738	0.192	3.32	2.710	0.170	3.20	2.682	0.178	2.91
	0.08003	3.087	0.335		3.065	0.304		3.018	0.273		2.975	0.223	
	0.11540	3.338	0.384		3.312	0.363		3.286	0.334		3.258	0.286	
	0.14820	3.537	0.438		3.478	0.386		3.393	0.340		3.367	0.319	

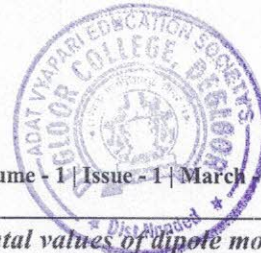


Table 2 The values of Debye constant (C), Kalman's factor (C') experimental values of dipole moment (μ exp.) and calculated values of dipole moment (μ cal.) of $nBA + EDA$ mixture in dilute solution of 1,4-dioxan at different temperature.


Solute %	$C \times 10^{-8}$	$C' \times 10^{-8}$	Temp. °K	μ exp. D	μ cal. D	μ^2 exp.	μ^2 cal.	% deviation in μ^2
nBA 100%	16.76	0.335	293	1.885	--	3.553	--	--
	19.32	0.326	303	1.924	--	3.701	--	--
	23.92	0.340	313	1.966	--	3.865	--	--
	29.06	0.329	323	2.000	--	4.000	--	--
nBA (69%) + EDA (31%)	17.04	0.291	293	1.827	1.823	3.338	3.326	-0.36
	19.84	0.285	303	1.864	1.862	3.475	3.467	-0.24
	24.26	0.291	313	1.905	1.903	3.630	3.621	-0.25
	30.55	0.289	323	1.940	1.937	3.763	3.752	-0.29
nBA (42%) + EDA (58%)	16.47	0.427	293	1.779	1.769	3.165	3.129	-1.15
	14.07	0.429	303	1.818	1.810	3.305	3.264	-1.25
	23.34	0.439	313	1.855	1.846	3.441	3.409	-0.94
	27.62	0.421	323	1.887	1.880	3.561	3.536	-0.70
nBA (20%) + EDA (80%)	14.05	0.375	293	1.730	1.723	2.993	2.970	-0.77
	14.87	0.339	303	1.764	1.762	3.112	3.098	-0.43
	17.42	0.339	313	1.802	1.799	3.247	3.237	-0.31
	20.75	0.327	323	1.830	1.833	3.350	3.360	0.30
EDA (100%)	8.47	0.162	293	1.673	--	2.844	--	--
	10.18	0.164	303	1.710	--	2.924	--	--
	12.30	0.167	313	1.765	--	3.112	--	--
	14.94	0.161	323	1.786	--	3.197	--	--

Table 3. The Values Of Free Energy Of Activation ($\Delta F_\tau, \Delta F_\eta$), Enthalpy Of Activation ($\Delta H_\tau, \Delta H_\eta$) And Entropy Of Activation ($\Delta S_\tau, \Delta S_\eta$) For nba, eda And Their Binary Mixtures In 1,4-Dioxan At Different Temperatures.

Solute %	Temp. °K	ΔF_τ	ΔH_τ	ΔS_τ	ΔF_η	ΔH_η	ΔS_η
		K cal/mole	K cal/mole	cal/mole	K cal/mole	K cal/mole	cal/mole
nBA (100%)	293	2.150	0.4677	-5.74	3.231	4.033	2.738
	303	2.218		-5.77	3.232		2.644
	313	2.302		-5.86	3.225		2.581
	323	2.363		-5.78	3.167		2.680
nBA (69%) + EDA (31%)	293	2.183	0.3256	-6.340	3.231	4.033	2.738
	303	2.234		-6.298	3.232		2.644
	313	2.311		-6.343	3.225		2.581
	323	2.368		-6.323	3.167		2.680
nBA (42%) + EDA (58%)	293	2.160	0.7038	-4.471	3.231	4.033	2.738
	303	2.210		-4.970	3.232		2.644
	313	2.287		-5.050	3.225		2.581
	323	2.300		-4.940	3.167		2.680
nBA (20%) + EDA (%)	293	2.069	0.7322	-4.562	3.231	4.033	2.738
	303	2.060		-4.382	3.232		2.644
	313	2.105		-4.386	3.225		2.581
	323	2.200		-4.544	3.167		2.680
EDA (100%)	293	1.78	0.429	-4.597	3.231	4.033	2.738
	303	1.83		-4.630	3.232		2.644
	313	1.89		-4.667	3.225		2.581
	323	1.91		-4.585	3.167		2.680

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