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DIELECTRIC BEHAVIOUR OF AMINE–ALCOHOL BINARY MIXTURES AT MICROWAVE FREQUENCIES

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ABSTRACT

The dielectric constant (ϵ') and dielectric loss (ϵ'') for binary liquid mixtures of diethylenetriamine + glycerine at 10.7 GHz microwave frequencies and temperature 22°C have been determined. Molar polarization, apparent polarization and the excess values of permitivities ($\Delta\epsilon'$, $\Delta\epsilon''$), square of refractive index ($\Delta\eta^2_D$), viscosity ($\Delta\eta$) and activation energy (Ea), were estimated from the measured dielectric data. The results suggest the formation of 1:2 complexes and strong interactions between the molecules of diethylenetriamine and glycerine.

Key words : Dielectric, Microwave, Diethylenetriamine, Glycerine

INTRODUCTION

Effects of molecular orientation are very sensitive to all kinds of interactions. Experimental investigation of dielectric properties of polar liquids from microwave absorption is of great value in understanding the nature of complex formation. In case of binary mixtures, the dielectric parameters, thermodynamic parameters, refractive index and viscosity do not vary linearly. The deviation from linearity of these parameters is called as excess parameters, which are useful to understand the nature of bonding between two constituents of the mixture.

The glycerine is used as sweetening agent in beverages, confectionery, in the preparation of soaps, cosmetics, inks, in preserving tobacco etc. Glycerine occurs in almost all natural animal fats and vegetable oils as the glycerol ester of higher organic acids. Thus the investigation on dipolar behaviour of glycerine is important in deciding its uses. The present work aims at the estimation of dielectric behaviour of diethylenetriamine, glycerin and their mixtures by studying the changes in the dielectric constant and loss factor ar toom temperature.

EXPERIMENTAL

Pure samples of diethylenetriamine (DETA) and glycerine (GLYN) were procured from M/s S.D. fine chemicals A.R. grade and used without further purification. The x–band microwave bench[1–4] was used to measure the wavelength in the dielectric. To hold the liquid sample in the cell, a thin mica window, whose V.S.W.R. and attenuation were neglected, is introduced between the cell and rest of the microwave bench. The dielectric constant ϵ' and loss

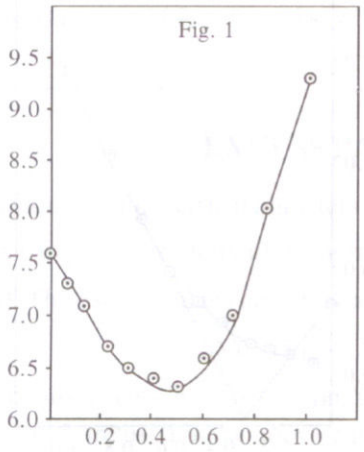
factor ϵ'' were measured by reflectometric technique[1–4] by measuring the reflection coefficient from the air – dielectric boundary of the liquid.

The dielectric constant (ϵ') and dielectric loss (ϵ'') for different mole fractions of DETA in the binary mixture of DETA + GLYN are measured at 22°C and 10.7 GHz microwave frequencies. In order to determine the dielectric wavelength (λ_d), attenuation per unit length ($\alpha_d \lambda_d$), dissipation factor (D), dielectric constant (ϵ') and loss factor (ϵ''), the movable short in the liquid cell was moved in and out and corresponding reflection coefficient was measured using the crystal detectors in the directional coupler. The relationship between the reflected power and depth of the liquid column is given by a damped sinusoidal curves. The distances between two adjacent minima of this curve gives $\lambda_d/2$. Thus knowing the values of λ_d, freespace wavelength (λ_o), cut off wavelength (λ_c) and $\alpha_d \lambda_d$, the values of parameters D, ϵ' and ϵ'' were determined by Serber's relations.4,5

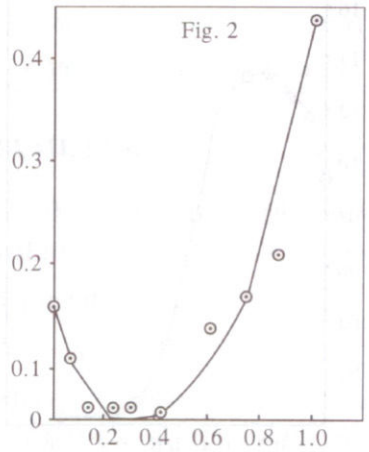
The density and viscosity of the pure components and their mixtures were measured by using the Pyknometer and Ostwald's Viscometer, respectively. Refractive indices for sodium D–line were measured by Abbe's refractometer.

RESULTS AND DISCUSSION

The dielectric constant (ϵ'), loss factor (ϵ'') loss tangent (tan δ), viscosity (η), square refractive index (n_D^2), activation energy (Ea) and molar polarization (P_{12}) with increasing mole fraction (X) of DETA for the binary mixtures of DETA + GLYN are reported in Table 1. The plot of the variation of the dielectric constant (ϵ') with molar concentration of DETA in the mixture is shown in Figure 1. A minima at X = 0.5 in the curve indicates the formation of complex in the binary mixtures of DETA + GLYN. Figure 2 indicates the microwave absorption in the mixture. A minima was observed in the tan δ versus mole fraction of DETA



Variation of ε versus x of DETA in the mixture



Variation of ε versus x of DETA in the mixture

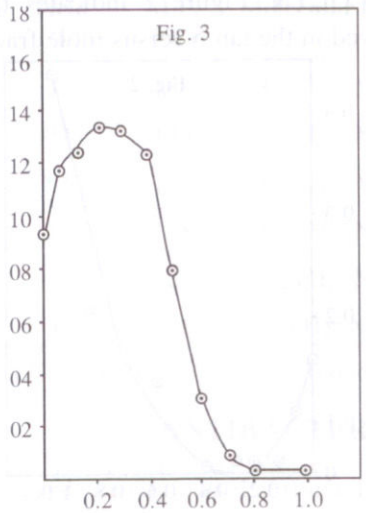
curve at X = 0.3. The nature of the curve suggests that the absorption in the mixtures is less than that in pure liquids. This is exactly opposite to the nature observed for amine–ketone binary mixtures by Singh and Sharma[5]. In the present study, the decrease in dielectric absorption in the binary mixtures suggests that the dipole moment (μ) and the relaxation time (τ) of the complex molecule decreases. Thus these differences of greater or less absorption in binary mixture arises from the geometry of complex[3]. Figure 3 indicates the plot of viscosity (η) with molar concentration of DETA in the mixture. The curve shows maxima at X = 0.24 mole fraction of DETA. Since in the present case, glycerine reacts with DETA by an exothermic reaction, the maxima for glycerine may be associated with the formation of dissociated ions in the mixture and the increase in (η) may also be attributed to the mutual visocity of the glycerine and amine molecules as provided by Andrade's theory[3].

Solution's molar polarization (P_{12}) is expressed as the weighted sum of the molar polarization's of the individual components. Thus,

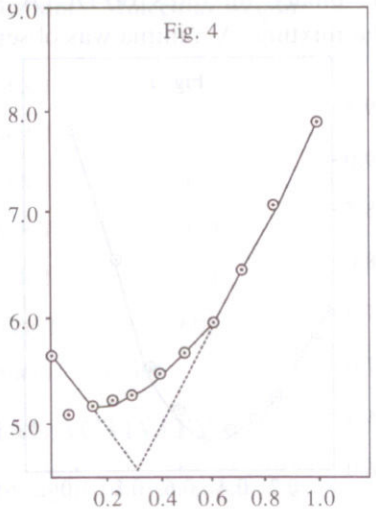
$$P_{12} = P_1X_1 + P_2X_2$$

$$= \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \frac{M_1X_1 + M_2X_2}{d_{12}}$$

Where M_1 and M_2 are the molecular weights, X_1 and X_2 are the molar concentrations of the constituents of the mixture and d_{12} is the density of the mixture. Subscripts 12, 1 and 2 refer to the solution, solvent and solute, respectively. Following Earp and Glasstone[6] and using the above formula, the values of P_{12}, P_1 and P_2 were calculated. The values of molar polarization P_{12} versus mole fraction (X) of DETA in the mixture are plotted in the Figure 4. The intersection of the straight lines is obtained at X = 0.3 mole fraction of DETA in the mixture.



Variation of η versus x of DETA in the mixture



Variation of P_{12} versus x of DETA in the mixture

The intersection point separates the low DETA concentration and high DETA concentration regions. The point of intersection X = 0.3 represents the point of maximum concentration of complex, which corresponds to a 1:2 complex for the system. This result regarding the formation of complex is supported by our earlier conclusions made from tan δ versus mole fraction curve. Figure 5 represents the variation of apparent polarization (P_2) for glycerine with mole fraction of glycerine in the mixture. According to Combs *et al.*,[7] flat curve indicates more stable complex. In the present case, curve shows that the complex is not much stable.

Table 1 : Values of mole fraction (*X*) of DETA, viscosity (η), square of the refractive index (n_D^2), dielectric constant (ϵ'), loss factor (ϵ''), loss tangent (tan δ), activation energy (*Ea*) and molar polarization (P_{12}) for DETA + Glycerine at 22°C.

X	ϵ'	ϵ''	tan δ	η (cp)	n_D^2	Ea Kcal/mole	P_{12} cm^3/mole
0.0000	7.6314	0.8117	0.1064	950.621	2.1697	7.4329	56.472
0.0695	7.348	0.4064	0.0577	1187.952	2.1786	7.5652	50.982
0.1439	7.169	0.0594	0.0088	1259.134	2.1934	7.5999	51.926
0.237	6.711	0.0532	0.0084	1347.79	2.2082	7.641	52.149
0.3095	6.551	0.0499	0.00812	1302.263	2.2112	7.620	53.509
0.4020	6.448	0.0033	0.00055	1238.217	2.2141	7.590	55.052
0.5021	6.396	0.1395	0.0231	799.933	2.2171	7.3295	57.266
0.6107	6.670	0.5740	0.0916	299.389	2.2141	6.7495	60.142
0.7289	7.086	0.7886	0.1180	92.142	2.2023	6.0408	65.268
0.8581	8.054	1.1992	0.1568	14.888	2.1993	4.9541	71.426
1.0000	9.320	3.496	0.3921	6.393	2.1845	4.450	79.419

EXCESS PARAMETERS

The excess values of dielectric parameters ($\Delta\epsilon'$)($\Delta\epsilon''$), excess viscosity (Δη), excess square refractive index (Δn_D^2), excess activation energy (ΔEa) for DETA + GLYN system is presented in Figures 6–10. The excess values are calculated using the following equation :

$$\Delta Y = Y_m - (X_1Y_1 + X_2Y_2)$$

where ΔY is any excess parameter and Y refers to the above mentioned quantities. The subscripts m, 1 and 2 are used in the above equation respectively for the mixture, component 1 and component 2. X_1 and X_2 are the mole fractions of two components in the mixtures. The

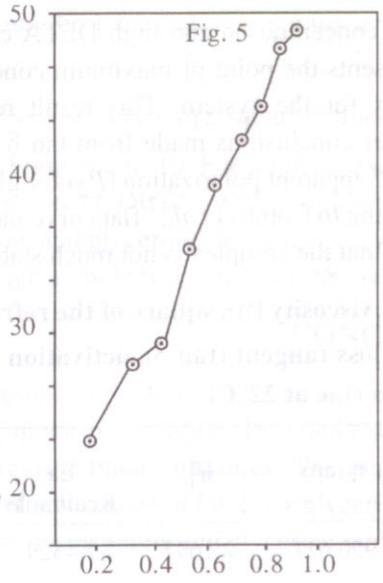


Fig. 5

Variation of P_2 versus x of DETA in the mixture

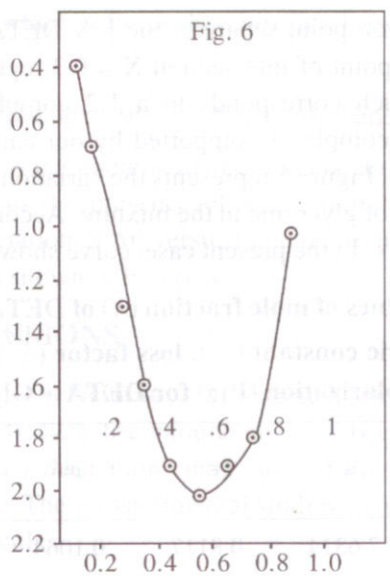


Fig. 6

Variation of $\Delta\varepsilon'$ versus x of DETA in the mixture

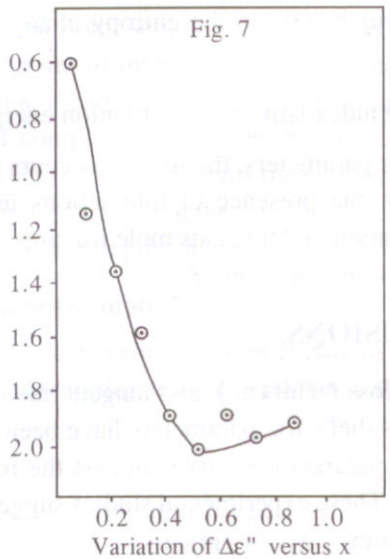
excess values were fitted through least squares with all points equally weighted by using Redlich–Kister equation[8]

$$\Delta Y = X_1 X_2 \sum_j Aj\,(X_1 - X_2)^j$$

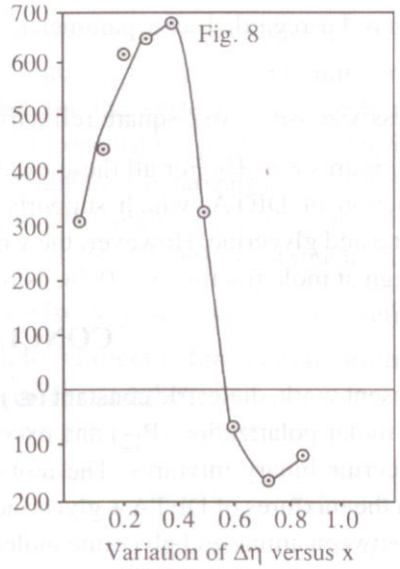
where Y is any physical parameter and X_1 and X_2 are the concentration of the two constituents. For better fitting curve, we have used six coefficient in the expansion. The values of coefficient A_j's for J = 0 to 5 are listed in Table 2 along with the standard deviation (σ). By using these Aj values excess parameters, ΔY were calculated and used as guidelines to draw smooth curves in Figures 6–10.

Table 2 : Values of coefficient A_j's and standard deviation (σ) in various excess parameters for DETA + Glycerine system at 22°C

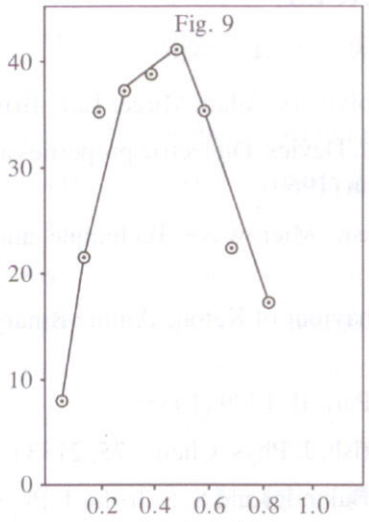
Physical parameter ΔY	A_0	A_1	A_2	A_3	A_4	A_5	σ
$\Delta\epsilon'$	–9.066	2.0941	5.0937	0.4368	4.034	3.7165	2.1590
$\Delta\epsilon''$	–7.7591	–0.6608	–1.891	–2.34	–13.985	–11.642	2.3126
$\Delta\eta$	471.01	–1869.155	12410.0	–4422.291	–20991.48	–2707.498	411.673
Δn^2_D	0.1541	–0.1076	–0.0132	0.0655	0.0362	0.19194	0.010961
ΔEa	5.444	–0.5654	–3.3896	–1.5448	–3.884	–6.3772	0.41746



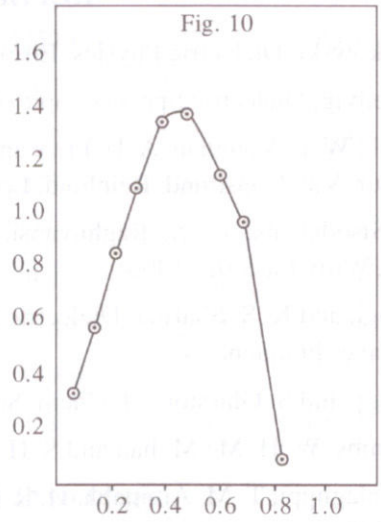
Variation of $\Delta\varepsilon''$ versus x of DETA in the mixture



Variation of $\Delta\eta$ versus x of DETA in the mixture



Variation of Δn_D^2 versus x of DETA in the mixture



Variation of ΔE_a versus x of DETA in the mixture

The excess dielectric constant ($\Delta\epsilon'$) and excess loss ($\Delta\epsilon''$) are negative. The minima in the $\Delta\epsilon'$ and $\Delta\epsilon''$ curves occur at 0.5 mole fraction of DETA in the mixture, where the formation of complexes was expected on the basis of ϵ', tan δ and η curves given in Fig. 1 to 3. $\Delta\epsilon' < 0$ indicates that the solute and solvent interact in such a way that the total effective dipoles get reduced. The solute and solvent may from multimers leading to the less effective dipoles. The excess permitivity $\Delta\epsilon'$ is associated with the polarization and the loss is regarded due to the molecular motions governed by the complex forces of molecular interactions. Thus, the excess

loss ($\Delta\epsilon''$) may be regarded as a parameter, which reflects the entropy change in a binary system.

The excess viscosity ($\Delta\eta$), square refractive index (Δn^2_D) and activation energy (ΔEa) are presented in Figures 8 to 10. For all these excess parameters, the maxima occurs at about X = 0.5 mole fraction of DETA, which supports to the presence of interactions in the system between amine and glycerine. However, the variation of $\Delta\eta$ versus mole fraction (X) of DETA changes its sign at mole fraction X = 0.58, as is shown in Figure 8.

CONCLUSIONS

In the present work, dielectric constant (ϵ'), loss factor (ϵ''), loss tangent (tan δ), activation energy (*Ea*), molar polarization (P_{12}) and excess dielectric parameters have been reported for DETA + glycerine binary mixtures. The molar polarization curve suggest the formation 1:2 complexes in the mixtures of DETA + glycerine. These experimental studies suggest the strong interactions between amine and glycerine molecules.

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