Dielectric studies of binary mixtures of *n*-propyl alcohol and ethylenediamine

B S NARWADE, P G GAWALI, REKHA PANDE and G M KALAMSE*

Department of Physics, Science College, Nanded 431605, India
e-mail: kalamse_gm123@rediffmail.com

Abstract. Dielectric constant (e') and dielectric loss (e'') of *n*-propyl alcohol (PA), ethylenediamine (EDA) and their binary mixtures, for different mole fractions of ethylenediamine have been experimentally measured at 11·15 GHz microwave frequency. Values of density (r), viscosity (h) and square refractive index (n_D^2) of binary mixtures as well as those of pure liquids are reported. Excess square refractive index, viscosity and activation energy of viscous flow have also been estimated. These parameters have been used to explain the formation of complexes in the system.

Keywords. Molecular interaction; binary mixture; dielectric parameters.

1. Introduction

Alcohols have found various applications[1] and commercial use in medical and other fields, for example *n*-propyl alcohol (PA) is very effective against a broad spectrum of microorganisms including bacteria, fungi and viruses such as HIV, hepatitis-B, and respirator syncytial viruses. Also *n*-propyl alcohol is in use as the safest antiseptic compound for topical use and is feedstock in the manufacture of insecticides. Therefore it seemed important to examine the dielectric behaviour of *n*-propyl alcohol with ethylenediamine (EDA).

Dielectric investigations of solutions containing varying amounts of interacting molecules help detect the formation and composition of complexes in them. A survey of the literature shows that a few workers[2–4] have tried to investigate some binary systems taking amines as one of the constituent components in the binary mixtures. Though the information in this field is steadily being enlarged by a number of workers,[2–5] the nature of complex formation in binary mixtures is still far from clear. With this in view, the present investigation is aimed at studying the dielectric behaviour of binary mixtures of *n*-propyl alcohol (PA) and ethylene diamine (EDA) which may provide useful information about the formation of complex in the mixture.

2. Experimental details

Pure samples of *n*-propyl alcohol (PA) and ethylenediamine (EDA) were procured from M/s SD Fine Chemicals, AR Grade and used without further purification. The two liquids were mixed in the required proportions by volume and kept in well-stoppered bottles to ensure good thermal equilibrium.

The viscosities and densities of the pure liquids and their mixtures were measured by using Oswald's Viscometer and Pycknometer respectively. The refractive indices at the sodium-D lines were measured by using Abbe's refractometer. The dielectric constant (e') and dielectric loss (e'') were measured by using Surber's technique[6] at 11·15 GHz microwave frequency and temperature 27°C.

The liquids for which dielectric properties were to be determined were taken in dielectric cells. A thin mica window, whose VSWR and attenuation were assumed to be negligible, was introduced between the cell and the rest of the microwave bench. The movable short plunger of the liquid cell was moved in and out, and the corresponding reflection coefficient $|\Gamma|$ was measured by means of a crystal pickup in the directional coupler. The plunger position (X) and the corresponding reflected output power gives sinusoidal damped waves. The distance between two adjacent minima or maxima of this curve gives wavelength (l_d) of radiation in the dielectric.

The experimental set-up and the procedure employed for the measurement of dielectric constant (e')

*For correspondence

and dielectric loss (e''), were the same as reported by Singh and Sharma.[4]

Surber[6] has derived the following relations for the dielectric parameters.

$$e' = \left(\frac{l_0}{l_c}\right) + \left(\frac{l_0}{l_d}\right)\left[1 + \tan^2\left(\frac{1}{2}\tan^{-1}D\right)\right] \quad (1)$$

and

$$e'' = \frac{1}{p}\left(\frac{l_0}{l_d}\right)^2 a_d l_d, \quad (2)$$

where a_d is the attenuation constant due to dielectric, l_d is the wavelength of the electromagnetic wave in the wave guide filled with dielectric, $l_c = 2a$ is the cut off wavelength for the wave guide, l_0 is the free space wavelength and $a_d l_d$ is the attenuation per wavelength and D is the dissipation factor. Having determined $a_d l_d$, l_0, l_c and l_d the values of e', e'' may be calculated by using the (1) and (2).

The free energy of activation (E_a) of the viscous flow for pure liquids and their mixtures is obtained by using the relation.[7,8]

$$h = (hN/V)\exp(E_a/RT) \quad (3)$$

The values of polarization of the mixtures were obtained using the formula[7,9]

$$P_{12} = (e'-1)/(e'+2)(X_1M_1 + X_2M_2)/d$$
$$= X_1P_1 + X_2P_2 \quad (4)$$

where M_1 and M_2 are the molecular weights, X_1 and X_2 the molar concentrations of the constituents of the mixture and d the density of the mixture.

3. Result and discussion

The values of viscosity (h), square of the refractive index (n_D^2), dielectric constant (e'), loss factor (e''), loss tangent ($\tan d$), and activation energy (E_a) for the viscous flow with increasing mole fraction (X) of EDA in the binary mixture of PA + EDA are listed in table 1.

Variation of dielectric constant (e') with molar concentration (X) of EDA in the mixture is depicted in figure 1. According to Job[10] if the relationship observed between (e') and mole fraction (X) for one of the components is not linear, there is an occurrence

of complexation and the curve of dielectric constant (e') against mole fraction (X) shows a change in slope at the mole fraction corresponding to the complex. In our present investigation of PA + EDA, binary mixture, the change in slope occurs at mole fraction $X = 0.44$ of EDA, hence the complex is at its greatest concentration at point $X = 0.44$. indicating the formation of a 1 : 1 complex;

The values of $\tan d$ in table 1 indicate that the microwave energy absorption in the mixture is greater than that in the pure liquids. Large energy absorption occurs approximately at equimolar ratio of the mixture which suggests an interaction-causing association between two types of molecules.

The viscosity curve indicates that the solute–solute interactions between PA and EDA increase to a maximum value around 0.44 mole fraction of EDA. Therefore it seems reasonable to assume that the formation of associates composed of PA and EDA in this composition range is held together by comparatively stronger intermolecular dipole–dipole interactions. The increase in viscosity (h) may also be attributed to the mutual viscosity of the alcohol–amine molecules as per by Andrade's theory.[7] Beyond the mole fraction 0.44 of EDA the viscosity
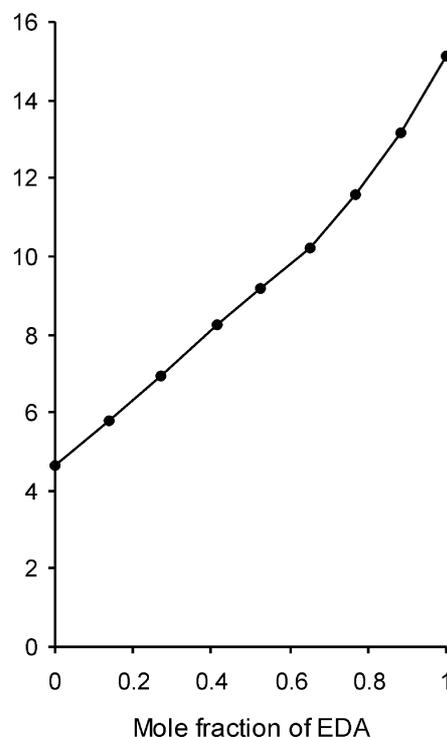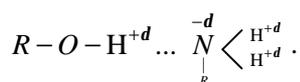

Figure 1. Variation of dielectric constant v/s mole fraction of EDA.

Table 1. Values of various parameters of binary liquid mixtures of *n*-propyl alcohol and ethylenediamine at 27°C.
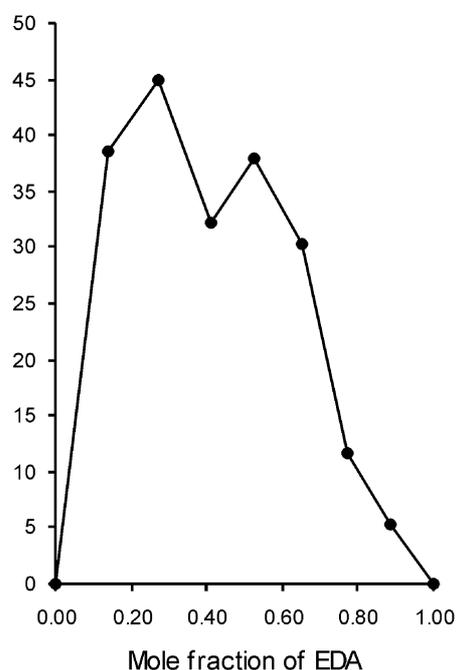
Mole fraction of EDA (X)	h (cP)	n_D^2	e'	e''	tan$d$	E_a (kcal/mole)
0·0000	1·218	1·918	4·629	0·080	0·017	3·173
0·1375	1·444	1·988	5·812	0·393	0·067	3·274
0·2711	1·471	2·025	6·908	0·314	0·0455	3·285
0·4143	1·497	2·045	8·246	1·936	0·234	3·296
0·5274	1·392	2·076	9·154	2·114	0·231	3·252
0·6502	1·279	2·096	10·231	2·283	0·223	3·202
0·7700	1·222	2·105	11·581	1·835	0·158	3·175
0·8865	1·142	2·128	13·185	1·249	0·094	3·134
1·0000	1·052	2·146	15·114	0·573	0·038	3·085
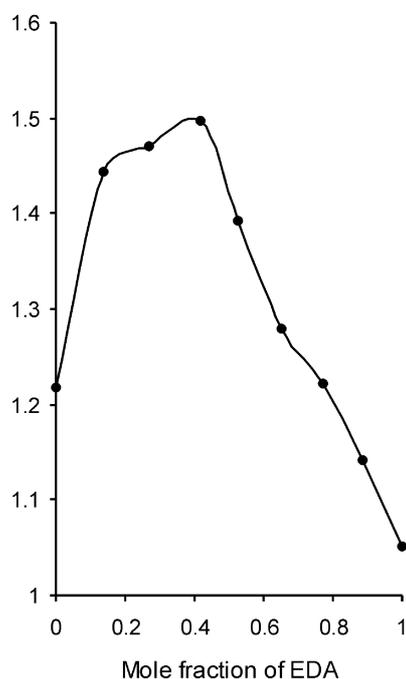
Figure 2. Variation of viscosity versus mole fraction of EDA.

Figure 3. Variation of excess square refractive index versus mole fraction of EDA.

values decreases (figure 2). Here we may expect the disruption of PA + EDA association with increase in the EDA component in the mixture. The following type of dipole–dipole association arising from the fractional negative charge on the nitrogen of the amine molecule and the fractional positive charge on hydrogen of the alcohol molecule can be proposed,

$$R - O - H^{+d} \ldots \overset{-d}{N} \Big\langle \begin{smallmatrix} H^{+d} \\ H^{+d} \end{smallmatrix} \;.$$

The possibility of linkage between the oxygen of alcohol and the hydrogen of amine is likely to be prevented due to steric hindrance, because of the

location of hydrogen in amine and that of oxygen in alcohol. Linkage between oxygen of alcohol with nitrogen of amine is not possible because the difference in the electronegativity levels of oxygen and nitrogen is too small (0·5) to merit any complexation. Hence complex formation is favoured in case of H^{+d} of alcohol and N^{-d} of amine in the manner represented above.

Excess values of square of refractive index (Δn_D^2) and activation energy (ΔE_a) for the system PA + EDA are shown in figures 3 and 4. The excess values were calculated by using the relation.
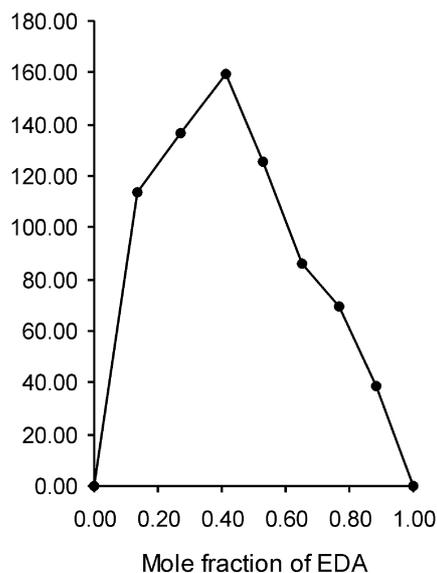
$$\Delta Y = Y_m - (X_1 Y_1 + X_2 Y_2), \tag{5}$$

Figure 4. Variation of excess activation energy versus mole fraction of EDA.

where ΔY is any excess parameter and Y refers to above mentioned quantities. The subscripts $m = 1$ and 2 used in the above equation are respectively for the components 1 and 2. X_1 and X_2 are the mole fractions of the two components in the liquid mixtures. The excess activation energy ΔE_a and excess square refractive index Δn_D^2 are positive, indicating the strong interactions between alcohol and amine molecules. For all these excess parameters, the maxima for the PA + EDA mixture occur at about 0·44 mole fraction of EDA.

4. Conclusion

Values of dielectric parameters, viscosity, activation energy and excess activation energy, and squares of refractive indices have been reported for different mole fractions of EDA in the binary mixture of PA + EDA. These studies suggest the strong interactions between *n*-propyl alcohol and ethylenediamine molecules. Dielectric constant and viscosity curves suggest formation of a 1 : 1 complex in the binary mixture.

Acknowledgement

References

1. Martindale J and Reynolds F F 1982 *The extra pharmacopoeia* 28th edn (London: Pharmaceutical Press)
2. Chelliah N and Sabesan R 1994 *Indian J. Pure Appl. Phys.* **32** 425
3. Tripathy S, Roy G S and Swain B B 1993 *Indian J. Pure Appl. Phys.* **31** 828
4. Singh P J and Sharma K S 1996 *Pramana – J. Phys.* **46** 259
5. Ali A, Nain A K, Dineshchand and Lal B 2003 *Indian J. Pure Appl. Phys.* **412** 928
6. Surber W H 1948 *J. Appl. Phys.* **19** 514
7. Hill N E, Vaughan W E, Price A H and Davis M 1968 *Dielectric properties and molecular behaviour* (London: Van Nostrand Reinhold)
8. Chelkowski A 1980 *Dielectric physics* (Amsterdam, Oxford, New York: Elsevier)
9. Earp D P and Glasstone S 1935 *J. Chem. Soc.* 1709
10. Job P 1928 *Ann. Chim.* **9** 113
11. Aralaguppi M I, Aminabhavi T M, Balundgi R H and Joshi S S 1991 *J. Phys. Chem.* **95** 5299