Chem Sci Trans., 2013, **2(2),** 677-683
DOI:10.7598/cst2013.430

Chemical Science Transactions
ISSN/E-ISSN: 2278-3458/2278-3318

RESEARCH ARTICLE

Excess Dielectric Properties of the Binary Liquid Mixture of 2-Chloroaniline + Ethylene Glycol at 10.985 GHz Microwave Frequencies

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Received 29 October 2012 /Accepted 12 November 2012

Abstract: The excess parameters studies in the microwave frequency region (X-band) on complex dielectric permittivity for the binary mixture are reported. The method employed adjustable plunger cavity technique. The values of dielectric permittivity (ε'), dielectric loss (ε'') have been experimentally determined for binary liquid mixture of 2-Chloroaniline+Ethylene glycol (2CA+EG) at 10.985 GHz microwave frequency at 23.8 ^{0}C. The values of ε' and ε'' have been used to evaluate the loss tangent (tan δ), molar polarization (P_{12}) activation energy (Ea) and excess permittivity ($\Delta\varepsilon'$), excess dielectric loss ($\Delta\varepsilon''$), excess molar polarization (ΔP_{12}), excess activation energy (ΔEa), excess refractive index (ΔRI) and excess viscosity ($\Delta\eta$) of viscous flow have also been estimated. These parameters have been used to explain the formation 2:1 complex in the system.

Keywords: Excess dielectric parameters, Binary mixture, Molar polarization, Intermolecular interaction

Introduction

It is well known that the thermophysical properties, of liquid systems such as density, viscosity, dielectric constant, refractive index among others, are strictly related to the molecular interactions present in different binary liquid mixtures. The variation of these properties with composition gives us important data about intermolecular interactions and the structure of pure and binary mixture of 2CA+EG. There is a wide range of possible interactions between the components of a mixture, such as hydrogen bonding, molecular associations, charge transfer, dipole-dipole and dipole-induced dipole interactions[1,2]. As a consequence of these interactions, deviations occur from ideal behavior of dielectric permittivity and viscosity. These deviations can be defined by excess dielectric permittivity. Experimental data on excess dielectric permittivity ($\Delta\varepsilon'$), excess dielectric loss ($\Delta\varepsilon''$), excess molar polarization (ΔP_{12}), excess viscosities ($\Delta\eta$), excess activation energy (ΔEa) and excess refractive index (ΔRI). Mixture of 2-chloroaniline with aliphatic diols are considerable from the view point of the existence of some interaction, such as hydrogen bonding between aniline which contain –NH_2 group and can act as a π-type donor and glycol molecules, which have two acidic hydrogen atom on the –OH group and can act a σ-acceptor.

$$\begin{array}{ccccccccccccc} & \mathrm{H} & & & & & & & & & \mathrm{H} & & \\ & |\,\delta- & & \delta+ & & & & & \delta+ & & \delta-\,| & & \\ C_6H_5 - & \mathrm{N} & \ldots & \mathrm{H} & -\mathrm{O}- & CH_2 & - & CH_2 & -\mathrm{O}-\mathrm{H} & \ldots\ldots & \mathrm{N} & - C_6H_5 & \\ & | & & & & & & & & & | & & \\ & \mathrm{H} & & & & & & & & & \mathrm{H} & & \end{array}$$

The aim of the present work is to determine excess properties of 2CA+EG at 23.8 ^{0}C and correlate these values with carbon chain length and intermolecular interactions.

Experimental

2-Chloroaniline (GC Grade) from Merck Schuchardt, Germany and Ethylene glycol (AR Grade) were obtained from Spectrochem PVT.LTD. Mumbai. India. Without further purification the two liquids according to their proportions by volume were mixed well and kept 6 h in well stoppered bottles to ensure good thermal equilibrium. 2CA is used as solute and EG as solvent.

Measurements

The dielectric constant (ε') and dielectric loss (ε'') have been measured using microwave X-band bench oscillating frequency of 10.985 GHz at 23.8 ^{0}C using source of Reflex klystron 2 K 25 (USSR) by Surber[3]. The densities and viscosities of the pure components and their mixtures were measured by using DMA 35 portable vibrating density meter. Anton paar Autria (Europe) having accuracy of density 0.001 g/cm^3 and viscosity by LVDL, V-pro II Brook field viscometer (USA).

A plunger waveguide is converted into a cavity by introducing a coupling hole in the entrance and shorting the other end with the calibrated plunger. The sample occupies the entire volume of the cavity. The frequency is kept constant and the length of the plunger cavity is changed. Hence several nodes appear as one increase the length of the cavity plunger. Whenever the length of the cavity equals the half integral multiples of the guide wavelength inside the medium, the plunger waveguide resonates. The distance through which the plunger is move between two successive cavity nodes gives half of the wavelength (λ_d) of the microwave inside the medium. The measurement of reflected power at resonance gives the attenuation coefficient of the sample[4].

Refractive indices for sodium *D*-line were measured by using Abbe's refractometer, having accuracy up to the third place of decimal microwave power measured by PM-437 (Attest) power meter, Chennai, India. Rectangular wave guide working TE_{10} mode, 10 dB, Vidyut Yantra Udyog, India. To hold the liquid sample in the liquid cell, thin mica window whose VSWR and attenuation were neglected is introduced between the cell and rest of microwave bench. The values of ε' and ε'' for low loss liquids are calculated according to Heston *et al.*[5] formula.

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

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

Where λ_c is the cut-off wavelength, λ_0 is the free space wavelength, λ_d is the wavelength in dielectric medium, λ_g is the wavelength in empty wave guide parameters and ρ is inverse voltage standing wave ratio.

Results and Discussion

The values of density (ρ), viscosity (η), refractive index (n), dielectric permittivity (ε'), dielectric loss (ε"), loss tangent (*tan* δ), activity energy (Ea) and molar polarization (P_{12}) for viscous flow with increasing mole fraction (X) of 2 CA for the binary mixtures of 2CA+EG are reported in Table 1.

Table 1. Values of mole fraction (X) of 2 CA density (ρ), viscosity (η), refractive index (n), dielectric constant (ε'), dielectric loss (ε"), loss tangent (*tan* δ), activation energy (E_a) and molar polarization (P_{12}) for binary liquid mixture at 23.8 ^{0}C

(2-Chloroaniline+ethylene glycol)

X	ρ gm/cm^3	η CP	n	ε'	ε"	tan δ	Ea, Kcal/mol	P_{12}
0.0000	1.109	14.1	1.417	40.213	0.6224	0.01548	4.8511	32.1668
0.07026	1.1257	12.9	1.439	4.777	0.4308	0.09032	4.7986	31.0728
0.14990	1.138	11.7	1.458	4.777	0.4308	0.09032	4.7410	33.8115
0.24093	1.1512	10.1	1.475	4.777	0.4308	0.09032	4.6543	36.9865
0.34598	1.1643	8.77	1.493	5.5362	0.5478	0.0989	4.5710	53.7169
0.46856	1.1753	6.81	1.512	4.1620	0.3449	0.0828	4.4218	41.4594
0.61345	1.1872	5.13	1.533	3.9041	0.3105	0.0795	4.2547	44.3149
0.78737	1.1981	3.45	1.556	4.1620	0.3449	0.08288	4.0207	51.9433
1.0000	1.209	3.321	1.575	40.5521	0.3993	0.08772	3.8717	62.5309

The excess parameters were calculated by the formula defined by Payne and Theodorou[6].

$$\Delta Y = Y_m - \left(X_1 Y_1 + X_2 Y_2 \right) \tag{3}$$

Where Y_m- is dielectric parameters for the mixture, Y_1 and Y_2 are the values for pure components, X_1 and X_2 are their respective molefraction. For ideal mixture, the excess parameters is zero, but real mixture have finite values. The excess may be positive or negative depending on complex formation.

Excess permittivity ($\Delta\varepsilon$')

Excess permittivity ($\Delta\varepsilon$') is a dielectric parameter, which gives information about the interaction between the components of mixture. Mehrotra *et at.*[7]. Had pointed out that the change in value of $\Delta\varepsilon$' with concentration is due to the interaction between dissimilar molecules which may produce structural changes. In present study, negative value of $\Delta\varepsilon$' are obtained for all concentration for 2CA + EG as shown in Figure 1. Indicates that the molecules in the binary mixture form multimers through hydrogen bonding in such a way that the effective dipole moments gets reduced[8]. It is observed that deviation in $\Delta\varepsilon$' is more negative at x=0.61345 mole fraction of 2CA.

Excess dielectric loss ($\Delta\varepsilon$")

The value of excess dielectric loss *($\Delta\varepsilon$")* is negative for 2CL + EG binary mixture. The minima occur at x=0.34598 mole fraction of 2CA as shown in Figure 2. The excess dielectric loss is regarded due to molecular motion which are governed by the complex forces of molecular interactions. Thus excess loss may be regarded as a parameter which reflects the entropy change in a binary system[9].

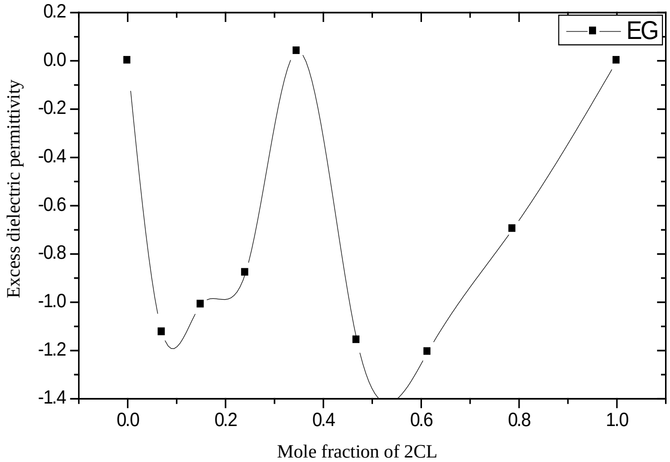

Figure 1. Plot of excess dielectric permittivity ($\Delta\varepsilon'$) with mole fraction of 2CA+EG

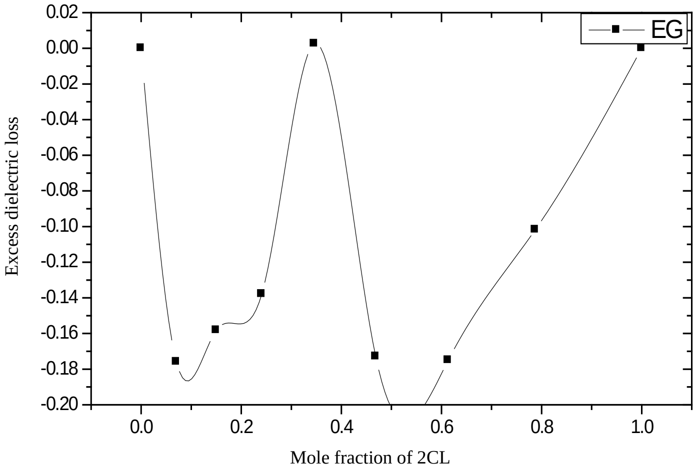

Figure 2. Plot of excess dielectric loss ($\Delta\varepsilon''$) with mole fraction of 2CA+EG

Excess activation energy (ΔE_a)

Positive value of excess activation energy indicates strong intersections between the 2CA and EG molecules. It is maximum at x=0.34598 mole fraction of 2CA as shown in Figure 3. The deviation of excess activation energy of viscous flow in these systems indicates the increase in the internal energy of the viscous flow. Thus supporting the presence of strong interactions in the system of 2CA and EG.

Excess viscosity ($\Delta\eta$)

The excess viscosity gives an estimation of the intermolecular interaction according to Ford and Moor, positive values of excess viscosity due to strong specific interaction causes complex formation and negative value of excess viscosity are observed for system of different molecular size in which the dispersion forces are dominant[10,11]. In our case the excess viscosity is negative as shown in Figure 4. Through the entire composition range for binary mixture under the investigation. The minimum excess viscosity is observed at x=0.6134 for the value of mole fraction where 2CA+EG. In order to explain we accept that the hydrogen bonds are broken and new species are formed. These new species consist of molecules having different geometrical configuration reaction.

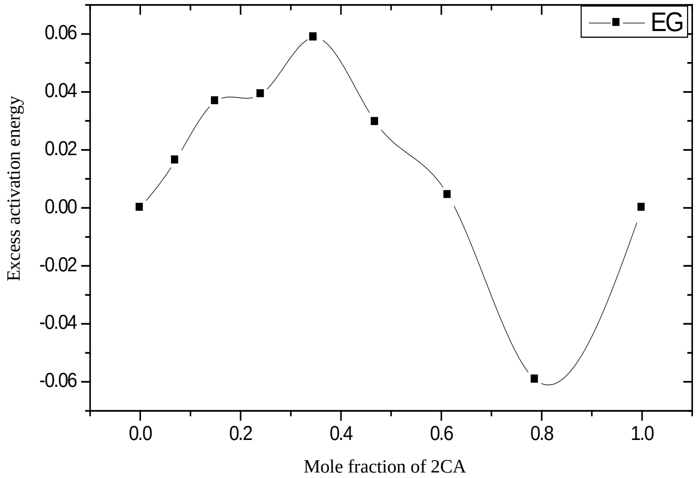

Figure 3. Plot of excess activation energy (ΔE_a) with mole fraction of 2CA+EG

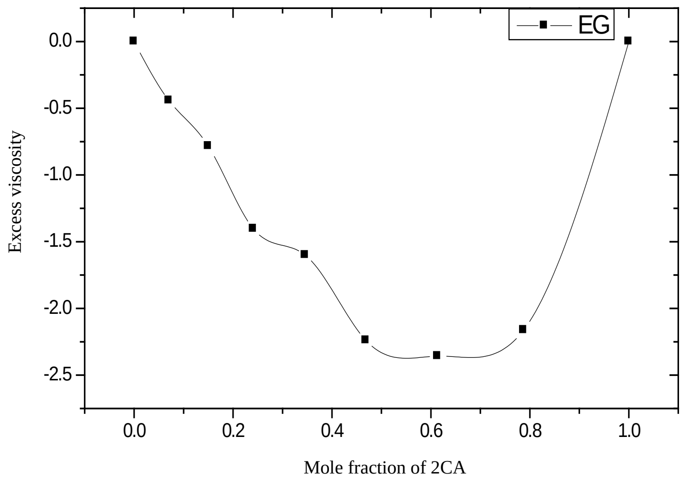

Figure 4. Plot of excess viscosity *($\Delta\eta$)* with mole fraction of 2CA+EG

Excess molar polarization (P_{12})

The value of excess molar polarization were negative over the entire range of 2CA + EG as shown in Figure 5. Negative deviation indicates dipole association, dipole induced dipole interaction or there is a decreases in hydrogen bonding with dilution. The 2CA + EG shows negative deviation from additinty at x=0.61345 mole fraction of 2CA which supports our earlier condition of the complex formation based on Figure 1 and Figure 4. This results regards the hydrogen bonding decreases is supporting by our earliear conclusion made from excess viscosity ($\Delta\eta$) *vs.* mole fraction curve according to Syrkin[12]. Excess molar polarization (P_{12}) is negative entire range of binary mixture.

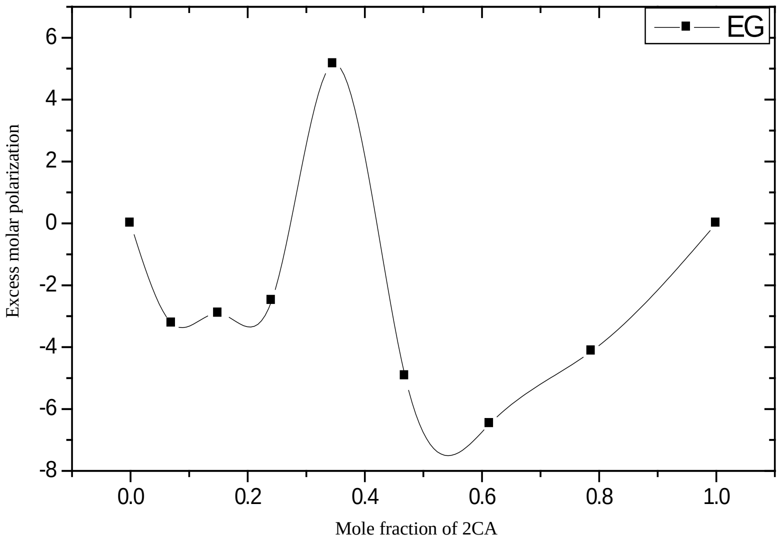

Figure 5. Plot of excess molar polarization (P_{12}) with mole fraction of 2CA+EG

Excess refractive index (ΔRI)

The values of excess refractive indices were positive over the entire range of mole fraction of 2CA+EG as shown in Figure 6. This is due to specific forces between molecules such as charge transfer complexes, intermolecular forces bringing positive excess values. Another aspect responsible for the values is the structural characteristics of the component arising from geometrical fitting of one component into other structure due to the differences in shape and size of the components and free volume. Excess refractive indices values are positive over the complete mole fraction range for binary mixtures indicates intermolecular interaction related to decrease in molar volume[13,14].

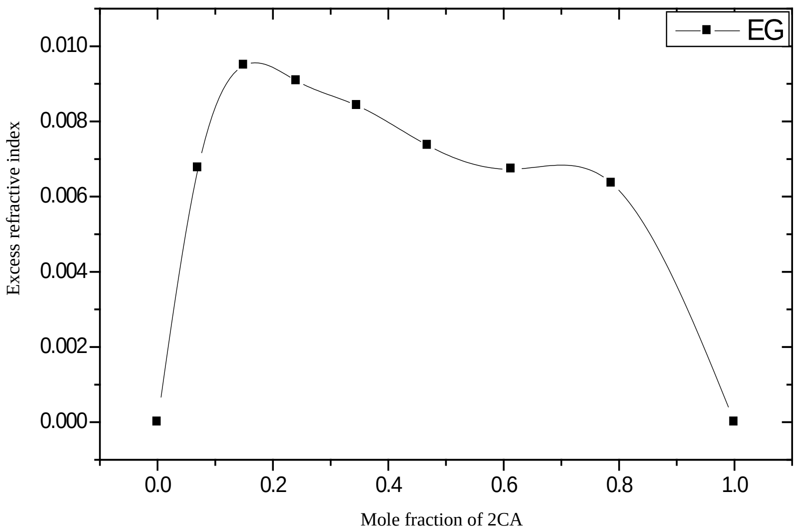

Figure 6. Plot of excess refractive index (*ΔRI*) with mole fraction of 2CA+EG

Conclusion

As can be understood from the above results, the excess properties of the studied mixture indicates some molecular interactions. Because of glycols are associate liquids, they can interact with each other and with 2-chloroaniline molecules. Dielectric constant and viscosity were the most affected parameters from these interactions. The excess values of these components exhibited a minima and maxima, which means a deviation from ideal behavior.

Acknowledgement

The authors are thankful to Dr. N.V.Kalyankar, Principal, Yeshwant Mahavidyalaya Nanded for providing necessary laboratory facilities.

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