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Dielectric Behaviour of Binary Mixture of 2-Chloroaniline with 2-Methoxyethanol at 30^0 C Using Microwave Frequency

Bhupesh G. Nemmaniwar

Digambarrao Bindu Arts, Commerce & Science College Bhokar Dist Nanded. M.S. India.

Abstract

Densities, viscosities, refractive indices, dielectric constant (ε') and dielectric loss (ε") of 2-Chloroaniline (2-CA)+2-Methoxyethanol (2-ME) for different mole fractions of 2-CA in binary mixture have been measured at single microwave frequency 10.985 GHz at 30^0C by Surber method using microwave X-band. The dielectric parameters ε' and ε" have been used to evaluate the molar polarization (P_{12}) loss tangent (tanδ), viscosity (η), activation energy (Ea).These parameters have been used to explain the formation of complexes in the system. It is found that dielectric constant (ε'), dielectric loss (ε"), loss tangent (tanδ), molar polarization (P_{12}) varies non-linearly but activation energy (Ea), viscosity (η), density (ρ), and refractiv index (n) varies linearly with increasing mole fraction in binary mixture of 2-Chloroaniline 2-CA+2-Methoxyethanol 2-ME. Hence, solute-solvent molecular associations have been reported.

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***Keywords**:* Molecular interaction, Polar liquids, Binary mixture, 2-Chloroaniline and 2-Methoxyethanol

1. Introduction:

Many studies on the fluid structures of polar and non polar mixtures have been reported [1]. Recently, there is an increased interest in the study of liquid mixture leading which leads to formation of hydrogen bonding in the system due to solute-solvent interactions during the recent times. Hydrogen bonding is complex in liquid state because of the uncertainty in identifying the particular bonds and the number of molecules involved. The presence of hydrogen bond brings a considerable change in the dielectric properties of liquid mixtures. Hydrogen bonds in 2-ME are responsible for the striking behavior, and in some instances provide evidence for the role of 2-ME in the sequence of chemical reactions. Hydrogen bonding in 2-ME is believed to be highly cooperative i.e. interaction of 2-ME molecules with a cluster of hydrogen bonded molecules is more likely than interaction with a single molecule to

* Corresponding author. Tel.: +91-9423306864;
E-mail address: bhupesh..nemmaniwar@rediffmail.com

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give a dimmer. Binary and ternary representations and prediction of intermolecular interactions with liquid dynamics by using reliable models. Dielectric studies on mixture of polar liquids either in pure state or in inert solvents have been a subject of interest because they provide useful information regarding the molecular complex formation in solution. Knowledge of frequency-dependent dielectric properties of binary liquid mixtures is important both in fundamental studies of solvent structure determination and its dynamics as well as in the practical applications. At a fundamental level, the frequency-dependent dielectric behavior of liquid mixtures provides information on molecular interactions and mechanism of molecular process. In pharmaceutical and analytical sciences, the dielectric constant of mixed solvents is required to predict the solubility and chemical stability of the drug [2]. Molecular mixtures bring about changes in thermodynamic properties like entropy, free energy and also in physical properties like density, molar volume, refractive index, dielectric permittivity etc [3].

2. Experimental

2-Chloroaniline (GC Grade) is obtained from Merck-Schuchardt, Germany. 2-Methoxyethanol Sigma Aldrich USA .Without further purification the two liquids 2-CA+2-ME according to their proportions by volume are mixed well and kept for 6 hours in well stoppered bottles to ensure good thermal equilibrium. These liquids are used as solute and solvent.

2.1 Measurements

The X-band microwave bench is used to measure wavelength in the dielectric medium and voltage standing wave ratio (VSWR) by using a short-circuiting plunger. The set up is tuned at microwave frequency 10.985 GHz. The experimental setup is shown in figure 1. The experimental techniques [4] for microwave measurements are used. All the measurements are carried out at temperatures 30^0C by circulating ethylene glycol + water around the dielectric cell and temperature is thermostically controlled with $\pm$ 0.5^0C using Nevitech pvt. Ltd. Mumbai India. The whole of the equipment is standardized with the help of standard materials like methanol and ethyleneglycol+water (40:60). Microwave power measured by PM-437 (Attest) power meter, Chennai, India using source of Reflex klystron 2 K 25 (USSR). The densities and viscosities of the pure components and their binary mixtures are measured by using DMA 35 portable vibrating density meter. Anton paar Autria (Europe) having accuracy of density 0.001 gm/cm^3, repeatability 0.0005 gm/cm^3 and resolution 0.0001 gm/cm^3 [5] and viscosity by LVDL, V-pro II Brook field viscometer with an accuracy of $\pm$1% (USA) [6]. 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 are neglected is introduced between the cell and rest of microwave bench. Refractive indices for sodium D-line were measured by using Abbe's refractometer that having accuracy up to the third place of decimal. The X-band microwave bench is used to measure wavelengths in the dielectric and the voltage standing wave ratio (VSWR). We determined the density ρ, viscosity η, refractive index n, dielectric constant ε', dielectric loss ε'', loss tangent tanδ, activation energy E_a and molar polarization P_{12} of dilute solutions of binary mixture of 2-CA+2-ME. All the measurements are carried out at temperatures 30^0C and the temperature is thermostatically controlled within $\pm 0.5^0$C. Microwave techniques have been used by method suggested [4]. To calculate dielectric constant ε', dielectric loss ε'' by the using the equations 1 and 2.

$$\varepsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \quad \text{……. (1)}$$

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

where λ_0, λ_c, λ_g and λ_d are the free space wavelengths, the cut-off wavelength, the waveguide wavelength and the wavelength in the waveguide filled with solution in centimeter respectively. ρ is the inverse of voltage standing wave ratio (VSWR) and dρ/dn is the slope of ρ versus n, where n=1,2,3….. Such that ($n\lambda_d/2$) represents the length of the dielectric filled waveguide. The precision of measurements for the wavelength with the available X-band microwave bench is $\pm 0.001 cm$ corresponding to this accuracy value, the error in the measurements of **ε'** is estimated. For simplification, involved errors due to non zero impedance of the short circuit plunger are ignored.

The relationship between the reflected power and depth of liquid columns is given by a damped sinusoidal curve. The distance between two adjacent minima of this curve gives λ/2. Thus the knowing the values of dielectric wavelength (λ_d), free space wavelength (λ_0), cut off wavelength (λ_c) and waveguide wavelength (λ_g) were determined by Surber relations [4]. To determined the **ε'** and **ε"** were measured by reflectometric technique by measuring reflection coefficient from the air dielectric boundary of the liquid [7]. The **ε'** and **ε"** for different mole fractions of 2-CA in the binary mixture of 2-CA+2-ME are measured at 30^0C. The free energy of activation (E_a) of the viscous flow for the pure liquids and their binary mixtures is obtained by using the following equation [8].

$$\eta = \left(hN / V\right) \exp\left(E_a / RT\right) \qquad \text{…….……. (3)}$$

Where η is the viscosity and V is the molar volume of the binary liquid and other symbols have their usual meaning. The molar polarizations of the binary mixture are obtained by using the formula [9].

$$P_{12} = \left(\frac{\varepsilon' - 1}{\varepsilon' + 2}\right)\left[\frac{M_1X_1 + M_2X_2}{\rho}\right] \qquad \text{…… (4)}$$

Where M_1 and M_2 are the molecular weight, X_1 and X_2 is the mole fraction of the constituents of the binary mixture.

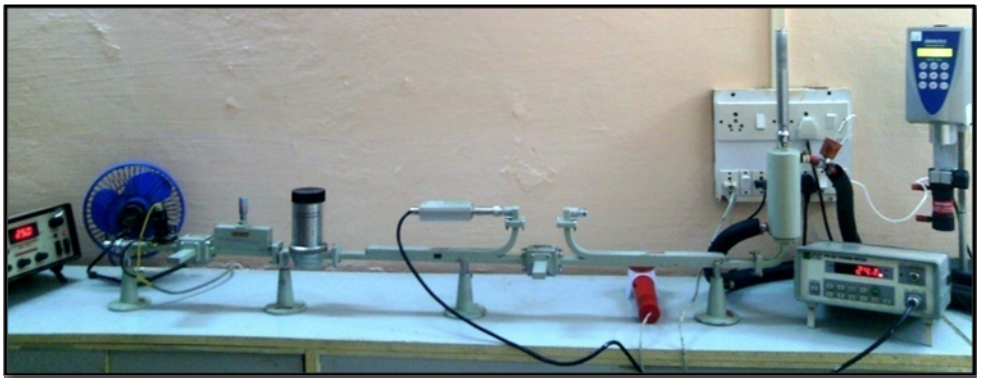

Fig. 1: The Experimental setup of X-band Microwave Bench

3. Results

The density (ρ), viscosity (η), refractive index (n), dielectric constant (ε'), dielectric loss (ε"), loss tangent (tanδ) , activation energy (E_a) and molar polarization (P_{12}) for viscous flow with increasing mole fraction (X) of 2-CA for the binary mixtures of 2-CA+2-ME are reported in tables 1 at 30^0C.

Table 1: Density (ρ), viscosity (η), refractive index (n),dielectric constant (ε'),dielectric loss (ε''), loss tangent (tanδ), activation energy (E_a) and molar polarization (P_{12})for binary mixture liquid system of 2-CA+2-ME at 30^0C.

X	ρ gm/cm^3	η CP	n	ε'	ε''	tanδ	E_a (Kcal/ mol)	P_{12}
0	0.9569	1.457	1.391	6.895	0.528	0.076	3.643	51.221
0.09647	0.9914	1.560	1.440	5.821	0.689	0.118	3.722	52.887
0.19944	1.0260	1.678	1.467	5.974	0.575	0.096	3.812	51.889
0.30959	1.0596	2.101	1.476	6.227	0.694	0.111	3.998	55.420
0.42771	1.0903	2.180	1.490	4.991	0.403	0.080	4.110	46.060
0.55469	1.1210	2.526	1.511	6.688	0.865	0.129	4.282	61.871
0.69156	1.1506	3.257	1.535	4.145	0.557	0.134	4.302	55.186
0.83953	1.170	4.172	1.547	4.145	0.397	0.095	4.404	54.007
1	1.2056	2.982	1.575	4.431	0.358	0.080	3.399	54.411

4. Discussion

According to [10] the dielectric constant may be used for the explanation of complexation in the mixture. If dielectric constant (ε') is plotted against the mole fraction of one of the component of a mixture, the nature of graph gives information regarding the occurrence of complexation. If the relationship observed is linear, then there is no occurrence of complexation.

On the other hand, if the relationship is non linear, then complex formation take place and complex is at its greatest concentration at a point of mole fraction where change in the slope is maximum. If the change in the slope occurs at a mole fraction of 0.5 then it indicates a complex of 1:1 type and if the change in slope occurs at a mole fraction of 0.7 then it indicates a complex 2:1. The variation between dielectric constant ε' and mole fraction X of 2-CA in the binary mixture of 2-CA+2-ME are reported in table 1. In this case ε' shows that nonlinearly vary which suggest the formation of H-bond complexes in these binary mixtures, over the entire concentration range. Deviations from linearity, indicating complex formation in the mixture as suggested [9]. From table 1 a pronounced minima is observed at X=0.4277 mole fraction of 2-CA in binary mixture 2-CA+2-ME which indicates the formation of 1:1complex in these binary mixtures as for the amines+alcohol mixtures observed [11]. The variation between loss tangent tanδ and mole fraction X of 2-CA is reported in table 1, which shows the absorption in the mixture is greater than that in pure liquid. The maxima in tanδ occurs at X=0.0964 mole fraction of 2-CA. In this case the formation of complex will increase the dielectric absorption due to the following consideration. In the complex, the dipole moment can be taken as ($\mu_{D1}+\mu_{D2}$), μ_{D1} and μ_{D2} being the dipole moment of constituent molecules. For n molecules of each liquid forming the complex absorption would be proportional to n ($\mu_{D1}^2+\mu_{D2}^2$), for pure liquids, assuming no interaction. On the other hand, in the mixture absorption would be proportional to the greater term n ($\mu_{D1}^2+\mu_{D2}^2$). The variation between molar polarization P_{12} and mole fraction X of 2-CA in the binary mixture of 2-CA+2-ME are listed in table 1. In our present investigation of 2-CA+2-ME binary mixture, which is responsible for multiple complextion in the binary mixture which shows the wobbling nature polarization maxima at X=0.5564 mole fraction of 2-CA and minimum at X=0.4277, which corresponds to 1:1 complex for the system. Thus this results regarding the formation of complex supported by our earlier conclusions made from variation between the ε' and mole fraction of 2-CA as in table 1. Similar results have been reported [9] for Aniline+2-ME, 2-EE, 2-BE.

5. Conclusions

In this case ε' shows that nonlinearly vary which suggest the formation of H-bond complexes in these binary mixtures, over the entire concentration range which indicates the formation of 1:1complex. In loss tangent tanδ formation of complex will increase the dielectric absorption, molar polarization which is responsible for multiple complextion in the binary mixture which shows the wobbling nature which corresponds to 1:1 complex for the syste

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