Evaluation of Molecular Interactions through Refractometric Study for Some Binary Liquid Mixtures

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ABSTRACT

Refractive index and density have been measured for binary mixtures of 2-(methoxycarbonyl)-1-propene with 2-methylpropan-1-ol and 2-methylpropan-2-ol at temperature 298K over the whole mole fraction range. From these data the excess molar volume, excess molar refraction and excess refractive index were calculated. These quantities are discussed in terms of intermolecular interactions.

Keywords: *Intermolecular interactions, refractive index, density, excess parameters.*

INTRODUCTION:

Thermodynamic and Refractometric data viz. refractive index, density, viscosity, speed of sound etc. and excess parameters like excess molar volume,excess molar refraction and excess refractive index etc. are very useful in various scientific research applications, engineering applications and in industries. Polar and non-polar organic liquid mixtures are of very important use as the study of physical and thermodynamic properties of these liquid mixtures gives very useful information at depth level about molecular interactions and other important aspects [1-5]. As far as the engineering and fundamental point of view is concerned it is very useful to have the knowledge about molecular interactions and structure of organic liquid mixtures. Actually organic liquid mixtures in comparison to pure organic liquids have many advantages for various industrial applications because mixing of these organic liquids gives flexibility to alter the various properties of pure organic liquids with the variation in concentration of these liquids [6-10]. With the study of pure liquids we cannot have the knowledge about certain properties like association and dissociation, complex formation, etc. this is because by mixing of these organic liquids we have very different types of phenomenon which are not exhibits by their individual pure components [11-14]. The idea of excess properties viz. excess molar volume V^E, excess molar refraction R^E, excess refractive index n^E etc. plays very important role here as this represents the difference between ideal and the actual properties of the systems. When molecules of solvent and solute interacts with each other it presents the non-ideal behaviour and this is responsible for interaction at molecular level among the components of organic liquid mixtures The study of importance of such mixing are studied by many workers[15-17]. There are number of techniques through which we can study about the molecular interactions and complex formation in organic liquid mixtures like ultrasonic investigation, viscometric investigation, refractometric investigation, dielectric, x-ray, vapour pressure, FTIR, and NMR,etc. but among these, refractometric investigation is one of the most authentic, easy and reliable method which requires comparatively very low experimental set up cost but at the same time can gives very useful and reliable knowledge about the interactions between molecules of components of organic liquid mixtures, about their arrangement and structural behaviour[18-21]. We are familiar that refractive index is among the physicochemical property of optically active substances. The refractive index of medium represents measure of the speed of light in that medium and is expressed as the ratio of phase velocity of electromagnetic wave in vacuum (c) to the velocity (v) in the medium under consideration for a given wavelength of electromagnetic wave. we can gather very useful information about optical medium or matter by studying behaviour of light for that medium. As a matter of fact we know that speed of light decreases accordingly when it passes through different substances in increasing refractive index order. This is due to molecular interaction inside those substances and also due to the effect of these interactions with light. As we increase the temperature of sample, the refractive index becomes decreases for most of the cases. Hence we can say that as temperature increases the interaction between molecules becomes changes [22]. We have taken 2-(Methoxycarbonyl)-1-Propene (MP) in present study which is one of the such organic liquid which have very useful role in engineering ,ophthalmology, dentistry, and industrial applications. Many researchers had taken this as binary mixture with other organic liquids because of its numerous advantages. [23-33]. Alcohols 2-Methylpropan-1-ol (M1) and 2-Methylpropan-2-ol (M2) are very

common to use as solvents among its other companions like ether, amines and water etc. Polar functional groups which are present in alcohol molecules make the alcohol as associated molecules. Molecule geometry, functional group position and carbon chain variational property are some properties due to which excess properties are very much influenced [34-38].In this paper, to investigate about molecular interactions through refractometric study and excess parameters, we have taken binary mixtures of (MP+M1) and (MP+M2) over the whole mole fraction range of MP at temperature 298K.

EXPERIMENTAL:

All the organic liquid samples taken in present study are of AR grade products. They are purified by standard methods [39-40]. Before performing measurements, all the samples were contained in dark bottles over 0.4 nm molecular sieves for reducing water part and made degassed using vacuum pump having nitrogen atmosphere. Chromatographic investigation was made to check the purities of organic liquids and mixtures on a molar basis, found purities were better than 0.995.Measurments were taken immediately after preparation of each component. By mixing of different volumes of two liquids; binary mixture was prepared in specially designed ground glass air tight ampoules after which it is weighed in single pan balance within the accuracy of 0.0001gm.Repeated measurements were taken to check the evaporation losses of solvent. Mole fraction was determined within the accuracy of ±0.0001.Abbe refractometer was used to measure refractive indices of pure organic liquid and liquid mixtures taken in this study. Inspection of scale was made with the help of test piece before measurements taken for refractive index using Abbe refractometer. Before each use, calibration of refractometer was done using distilled water. Thermostatically controlled water bath (accuracy ±0.01K) was used to maintain the temperature constant. Refractive indices measured here are accurate within the accuracy limit of ±0.0001.Organic samples and their mixtures were injected directly to the refractometer prism assembly using syringe. An average of three measurements was taken for each organic liquid and liquid mixture. Densities was measured with bicapillary pycnometer having bulb volume of $15cm^3$, internal diameter of capillary was 1mm.Density measurement was accurate to ± 0.00001gm cm^{-3} .Calibration of pycnometer was done with distilled water. Thermostatically controlled water bath(accuracy ±0.01K) was used to maintain the temperature constant. Thermal equilibrium was attained by giving adequate time to samples in water bath.

RESULTS AND DISCUSSION:

Experimental values of refractive index, densities and calculated values of excess molar volume V^E, excess molar refraction R^E and excess refractive index n^E over the whole mole fraction range of MP for binary mixtures of (MP+M1) and (MP+M2) at temperature 298K is given in Table-1 and Table-2 respectively. Values of excess molar volume V^E , excess molar refraction R^E and excess refractive index n^E for binary systems (MP+M1) and (MP+M2) at T=298 K are plotted with respect to whole mole fraction range and shown in Fig.1 , Fig.2 and Fig.3 respectively.General and expanded form of relations to compute excess molar volume, excess molar refraction and excess refractive index are given by equations as follows.

$$V^E = V - \sum_i V_i \, X_i$$

$$R^E = R - \sum_i R_i \, \phi_i$$

$$n^E = n_m - \sum_i n_i \, X_i$$

Where molar refraction R is given by relation

$$R = \frac{(n_m^2-1)}{(n_m^2+2)} V$$

Where $V = \frac{\sum_i X_i M_i}{\rho}$

$$V^E = \left(\frac{X_1M_1+X_2M_2}{\rho}\right) - \left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right)$$

$$R^E = \frac{(n_m^2-1)}{(n_m^2+2)} \left(\frac{X_1M_1+X_2M_2}{\rho}\right) - \left[\frac{(n_1^2-1)}{(n_1^2+2)} \frac{M_1}{\rho_1}\phi_1 + \frac{(n_2^2-1)}{(n_2^2+2)} \frac{M_2}{\rho_2}\phi_2\right]$$

$n^E = n_m - (x_1n_1+x_2n_2)$

Where $\phi_1 = x_1V_1 / \sum x_iV_i$

$\phi_2 = x_2 V_2 / \sum x_i V_i$

n_m = Refractive index of mixture

ρ = density of mixture

n_1 = Refractive index of pure component-1

n_2 = Refractive index of pure component-2

ρ_1 = density of pure component-1

ρ_2 = density of pure component-2

ϕ_1 = Volume fraction of pure component-1

ϕ_2 = Volume fraction of pure component-2

Here x_i is the mole fraction and V_i is the molar volume of component i.

The results of excess molar volume V^E for binary systems of (MP+M1) and (MP+M2) as a function of mole fraction (x_1) of MP at 298K temperature is presented in Figure-1. It shows that excess molar volume V^E have positive values for both the binary systems (MP+M1) and (MP+M2) over the entire range of mixture composition. Positive values of V^E may reflects that there exists lesser intermolecular interactions for both the binary systems (MP+M1) and (MP+M2).Breaking up of the liquid order i.e. intermolecular hydrogen bonding between alcohol molecules with possible new hydrogen bonding with molecules of other component of mixture may lead to positive values of V^E. Maxima for both the binary systems (MP+M1) and (MP+M2) occurs for same values of mole fraction of MP but value of excess molar volume for binary system (MP+M2) is comparatively high.

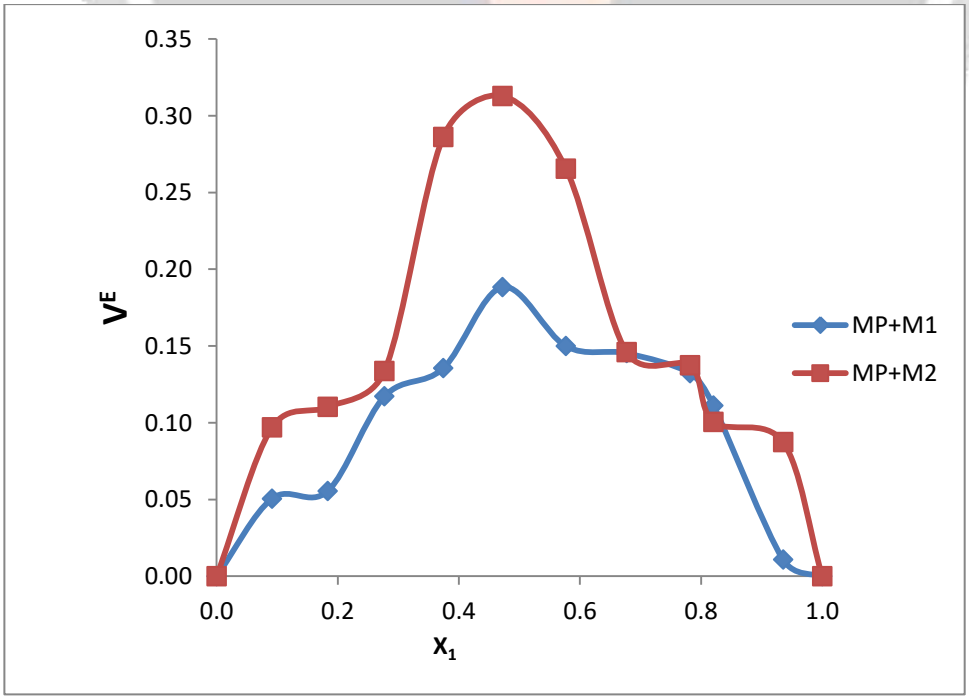

Figure-1 Excess molar volume vs. mole fraction for binary mixtures (MP+M1) and (MP+M2) at 298K.

This rapid increment in maximum value of V^E indicates that for this point system deviates very high comparatively. Values of V^E for higher side of mole fraction for both the binary systems coincide with each other. From this we may say that binary systems taken here shows very complex pattern. Excess molar refraction R^E represents the complex electronic perturbation between liquid components due to orbital mixing of components.The results of excess molar refraction R^E for binary systems of (MP+M1) and (MP+M2) as a function of mole fraction (x_1) of MP at 298K temperature is presented in figure-2. Excess molar refraction R^E have negative values for both the binary systems (MP+M1) and (MP+M2) over entire range of composition at temperature 298K.

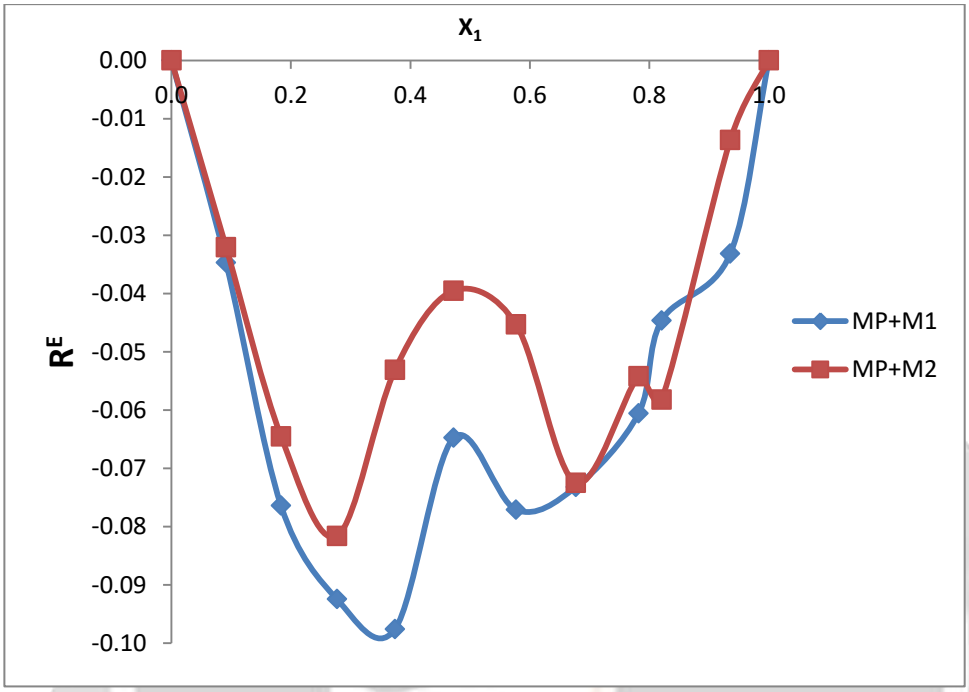

Figure-2 Excess molar refraction vs. mole fraction for binary mixtures (MP+M1) and (MP+M2) at 298K.

It is noticed that negative values of excess molar refraction R^E are very small for the entire composition range except for mole fraction value between 0.2 to 0.4. It is seen that for lower values of mole fraction, excess molar refraction R^E for both the binary systems (MP+M1) and (MP+M2) at 298K have similar values but as we move further for mid-range of mole fraction the order of negative values of R^E is (MP+M1) > (MP+M2). For further higher values of mole fraction, excess molar refraction R^E values for both the binary systems (MP+M1) and (MP+M2) exhibits abnormal complex behavior. Values of R^E for higher side of mole fraction for both the binary systems coincide with each other. As described earlier, similar observations was found for excess molar volume V^E also. The results of excess refractive index n^E for both the binary systems (MP+M1) and (MP+M2) as a function of mole fraction (x_1) of MP at 298K temperature is presented in figure-3.The excess refractive index n^E i.e. deviations in refractive index as a function of mole fraction for both the binary systems (MP+M1) and (MP+M2) shows the positive values over whole composition range. As we move over whole range of mole fraction the order of positive values of n^E is (MP+M1) > (MP+M2). It is clearly seen from figure-3 that for the whole mole fraction range, the deviations in values of refractive index are very-very low.

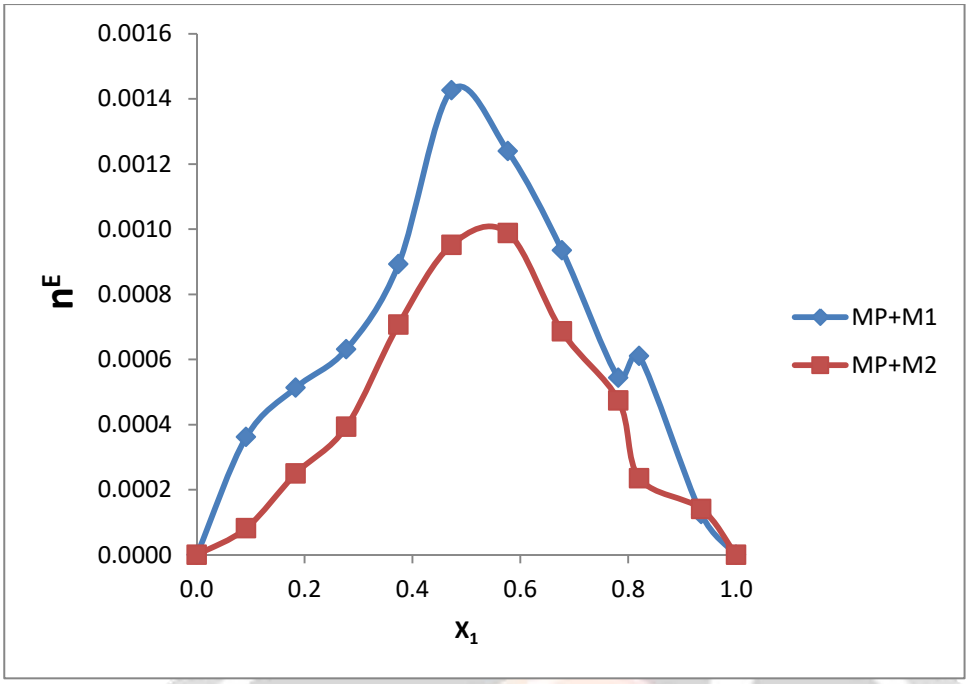

Figure-3 Excess refractive index vs. mole fraction for mixtures of (MP+M1) and (MP+M2) at 298K.

As we seen for excess molar volume V^E vs. mole fraction graph in figure-1, here also for both the binary systems (MP+M1) and (MP+M2) at 298K we have maxima for both the binary systems occurs at same value of mole fraction as seen in figure-3. Values of excess refractive index n^E for higher side of mole fraction for both the binary systems (MP+M1) and (MP+M2) at 298K almost coincides with each other. As described earlier similar observation was found for excess molar volume V^E and excess molar refraction R^E also.

Table-1 Refractive index (n_m),density (ρ),excess molar volume (V^E), excess molar refraction (R^E), excess refractive index (n^E) for binary mixture of (MP+M1) at temperature 298K as a function of the mole fraction x_1 of MP.

X_1	ρ	n_m	V^E	R^E	n^E
0.0000	0.7978	1.3931	0.0000	0.0000	0.0000
0.0915	0.8119	1.3952	0.0506	-0.0347	0.0004
0.1835	0.8260	1.3971	0.0555	-0.0764	0.0005
0.2773	0.8395	1.3990	0.1172	-0.0925	0.0006
0.3741	0.8535	1.4011	0.1355	-0.0976	0.0009
0.4723	0.8670	1.4035	0.1884	-0.0648	0.0014
0.5769	0.8818	1.4053	0.1499	-0.0771	0.0012
0.6771	0.8953	1.4069	0.1453	-0.0732	0.0009
0.7819	0.9091	1.4085	0.1323	-0.0606	0.0005
0.8205	0.9142	1.4093	0.1112	-0.0446	0.0006
0.9355	0.9295	1.4110	0.0108	-0.0332	0.0001
1.0000	0.9375	1.4121	0.0000	0.0000	0.0000

Table-2 Refractive index (n_m),density (ρ),excess molar volume (V^E), excess molar refraction (R^E), excess refractive index(n^E) for binary mixture of (MP+M2) at temperature 298K as a function of the mole fraction x_1 of MP.

X_1	ρ	n_m	V^E	R^E	n^E
0.0000	0.7811	1.3854	0.0000	0.0000	0.0000
0.0943	0.7967	1.3880	0.0970	-0.0321	0.0001
0.1854	0.8121	1.3906	0.1103	-0.0645	0.0002
0.2699	0.8259	1.3930	0.1337	-0.0816	0.0004
0.3855	0.8434	1.3964	0.2861	-0.0531	0.0007
0.4625	0.8554	1.3987	0.3129	-0.0395	0.0010
0.5585	0.8707	1.4013	0.2655	-0.0453	0.0010
0.6672	0.8882	1.4039	0.1459	-0.0725	0.0007
0.7725	0.9039	1.4065	0.1374	-0.0542	0.0005
0.8189	0.9109	1.4075	0.1005	-0.0582	0.0002
0.9273	0.9266	1.4103	0.0873	-0.0137	0.0001
1.0000	0.9375	1.4121	0.0000	0.0000	0.0000

CONCLUSIONS:

From above it may be concluded that binary systems taken in this study exhibits the positive values for excess molar volume but small negative values for excess molar refraction. These values represent complex mixing behaviour and molecular interactions between components of mixture for these binary systems.

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