Investigation and Analysis of Molecular Interactions through Refractometric and Excess Parametric Data of Binary Liquid Mixture

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ABSTRACT

Refractive index and density have been measured for binary mixtures of Dimethyl Carbinol with Propyl Ethanoate and Ethyl 2-Hydroxypropanoate 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:

Organic liquids and their binary or ternary mixtures are very important as study of these can provide a very valuable and deep knowledge for the molecular interactions between the molecules of a mixture and also provide information about molecular structure. In spite of pure organic liquids, their binary and ternary mixtures are very useful in determining the knowledge about the molecular interactions, molecular structure etc. and thus very largely used in various scientific and industrial applications [1-4]. When we take the mixture of any organic liquid with other, then the various physical properties get changed and they are considerably different from the original pure component properties. Knowledge about certain properties like association and dissociation, complex formation etc. cannot be studied through organic liquids in their pure state [5-7]. Physicochemical Properties of pure organic liquids and organic liquid mixtures viz. Viscosity, Density, Surface Tension, Refractive Index etc. and excess parameters viz. excess molar volume, excess molar refraction, excess refractive index etc. forms the very valuable data base in determining the various information about liquid and their mixtures which includes molecular interactions, molecular structure, molecular rearrangements etc. The advantage of this study is two-fold. At first, it imparts an indirect but convenient and easy method to explore the nature and possibilities of microscopic interactions between like and unlike molecules of liquid mixtures. Secondly, it constitute experimental background to compose, modify and investigate about the theories, models for the prediction of various properties of binary and ternary organic liquid mixtures. Lot of workers has made an attempt for this type of investigation [8-12]. For liquid mixtures, an ideal mixture is that whose parameters obey some very well defined standard rules. But standard model of ideality declines as per the category of system. Thus excess parameters plays, here, very important role as they can provide relatively convenient scale of new ideality for these liquid mixtures. They can be defined as differences between original and ideal mixture. Study of excess parameters such as excess molar volume, excess molar refraction and excess refractive index etc. are found to be very helpful in understanding the nature, structural behavior and order of molecular interactions in liquid mixtures [13-15]. There are some other parameters which can also give valuable information about above properties of liquid mixtures such as excess enthalpy, adiabatic compressibility, intermolecular free length, internal pressure etc. these are used by many workers in the field of ultrasonic and other techniques by many workers. There are various techniques and methods such as Viscometric, Refractometric, Ultrasonic, Dielectric, X-ray, Vapour Pressure, FTIR, and NMR, etc. to investigate about the nature, intermolecular interactions, molecular rearrangements and structural behavior of the binary and ternary organic liquid mixtures. Out of these various techniques and methods The Refractometric, Viscometric and Ultrasonic techniques are widely used because they requires comparatively easy handled low cost experimental set up and provides correct result as well. In the present work we employ the Refractometric technique to explore about the molecular interactions, molecular rearrangements, and structural information of components of binary liquid mixtures as it is performed by a lot of workers for a long time. Refractive index of an optically active medium is an important property of pure organic liquids and organic liquid mixtures, 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. Hence in medium of higher refractive index speed of light is accordingly low for that medium. This is due to molecular interactions inside that matter and due to effect of these interactions with light. With the increase in temperature of sample refractive index becomes decreases this further confirms about the changes in molecular interaction. Thus refractive index is very closely connected with the internal structure of matter and can give valuable information about molecular interactions. Organic spices taken in this study comprises of Dimethyl Carbinol (DC), Propyl Ethanoate (PE) and Ethyl 2-Hydroxypropanoate (EH). EH is a green solvent [16]. Green solvents are environment friendly solvents and are perfect alternative to petrochemical solvents. It is a perfect biodegradable solvent which has almost zero Eco toxicity [17]. EH has a high solvency power and is used widely in coating industry. It has replaced solvents such as acetone, xylene, and toluene [18]. DC is very common organic liquid used as solvent.it is also a type of green solvent. It is widely used in many industrial scientific and medical applications and in household chemicals as well. Hand sanitizer, disinfectants, antiseptics, and detergents etc. are few products in which it is used commercially. PE is also used widely in many scientific and industrial applications. It is also very common to use it as a solvent in industries and is used as a flavouring medium in foods as well. Wide variety of resins is dissolved with it thus make it perfect choice for coating industry. Organic liquid mixtures comprises of esters and alcohols are very commonly used to study the solute- solvent and solvent-solvent interaction properties of organic liquid mixtures[19-23] and hence finds its huge applications in chemical industries and for research purpose also. Refractometric and excess parametric study is carried out in this paper to investigate for interactions at molecular level with the help of binary mixtures of above mentioned organic liquids (DC+PE) and (DC+EH) over the whole mole fraction range of DC at 298K temperature.

EXPERIMENTAL:

In present study, AR grade products are taken for all the organic liquid samples. They are purified by standard methods as given in literature [24-25]. 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. Chromatographic investigation was made to check the purities of organic liquids and their binary mixtures on a molar basis; it is found that purities were better than0 .995.Measurments were taken just after preparation of each component. By mixing of different volumes of two liquids; binary mixture of organic liquids was prepared in specially designed ground glass air tight ampoules after which it is weighed in single pan balance which has the accuracy of 0.0001gm.Few 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 the refractive indices of pure organic liquid and their binary liquid mixtures taken here. Inspection of scale was made with the help of test piece before each measurement. Before each use, calibration of Abbe refractometer was done using distilled water. Refractive indices measured here are accurate within the accuracy limit of ±0.0001.Pure organic liquids and their binary mixtures were injected directly to the refractometer prism assembly using plastic syringe. An average of triplicate measurements was taken as final reading. Densities were 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 for binary mixtures of (DC+PE) and (DC+EH) 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 (DC+PE) and (DC+EH) 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 (DC+PE) and (DC+EH) as a function of mole fraction (x_1) of DC at 298K temperature is presented in figure-1. It shows that excess molar volume V^E have positive values for both the binary systems (DC+PE) and (DC+EH) 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 (DC+PE) and (DC+EH). For whole mole fraction range the values of V^E for both the binary system has order (DC+PE) < (DC+EH). Maxima for binary system (DC+EH) has relatively very high value in comparison to maxima for other binary system (DC+PE).Curve for (DC+EH) has very steep slope while for (DC+PE) has almost negligible slope in mid mole fraction region i.e. for 0.2 to 0.8 mole fraction values.

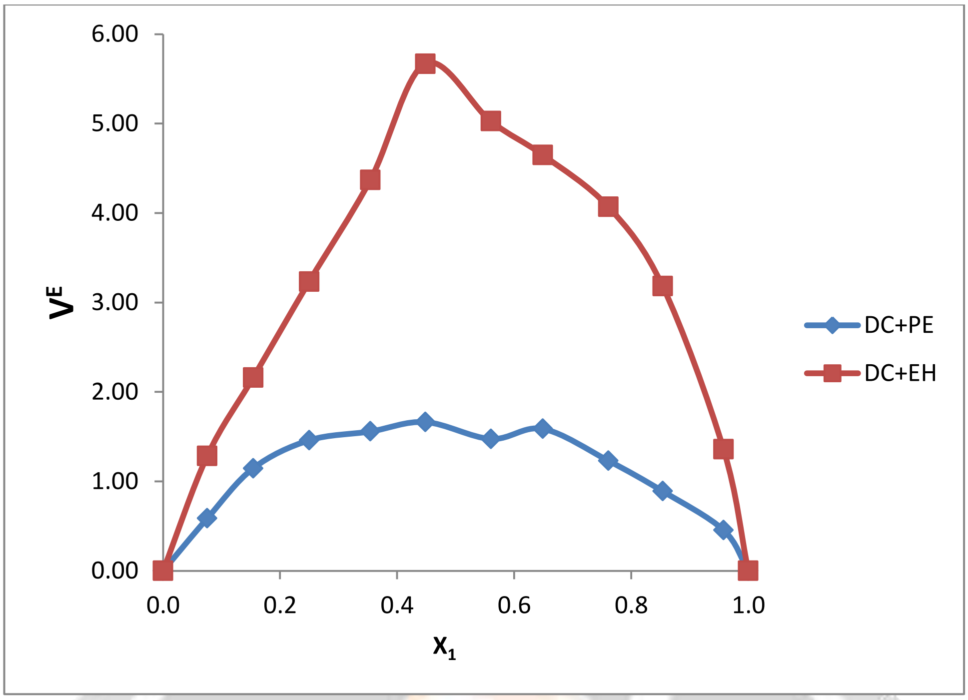

Figure-1 Excess molar volume vs. mole fraction for binary mixtures (DC+PE) and (DC+EH) at 298K.

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 (DC+PE) and (DC+EH) as a function of mole fraction (x_1) of DC at 298K temperature is presented in figure-2

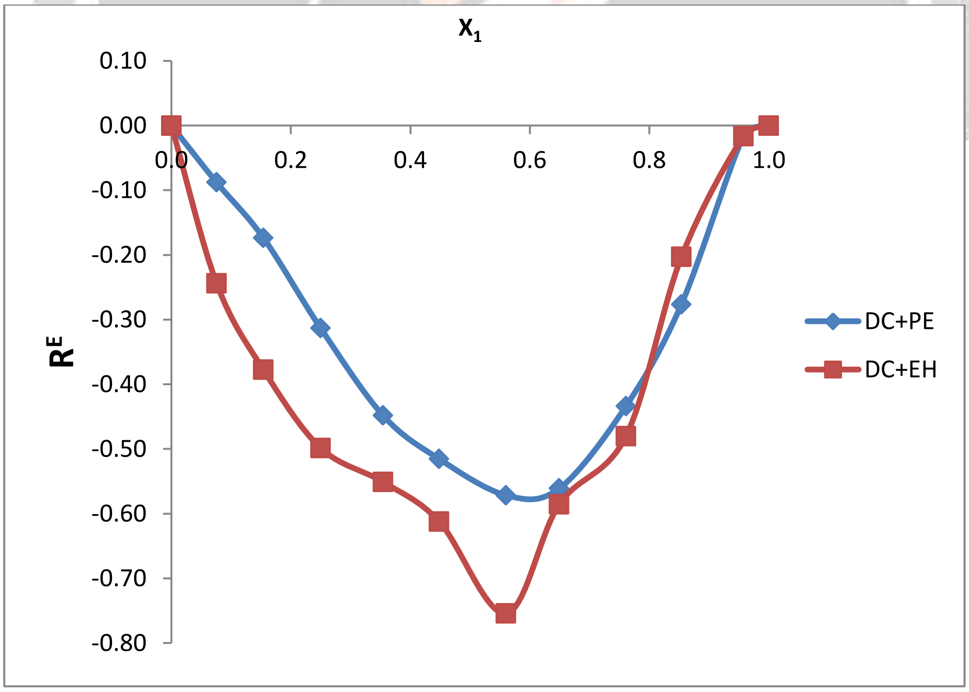

Figure-2 Excess molar refraction vs. mole fraction for binary mixtures (DC+PE) and (DC+EH) at 298K.

It shows that excess molar refraction R^E have negative values for both the binary systems (DC+PE) and (DC+EH) over the entire range of mixture composition at temperature 298K. It is seen that for lower values of mole fraction , excess molar refraction R^E for both the binary systems (DC+PE) and (DC+EH) at 298K have almost similar values but as we move further for mid-range of mole fraction the order of negative values of R^E is (DC+EH) > (DC+PE). Curve for binary mixture (DC+EH) is almost flat in mid of mole fraction region on the other side for binary mixture (DC+PE) curve is pointed at mid mole fraction range. The results of excess refractive index n^E for both the binary systems (DC+PE) and (DC+EH) as a function of mole fraction (x_1) of DC at 298K temperature is presented in figure-3.It is interesting to see that values of excess refractive index n^E i.e. deviations in refractive index for binary system (DC+PE) is positive for whole mole fraction range while for the binary systems (DC+EH) it has negative values for whole mole fraction range. It is also observed that for binary system(DC+EH) the values of excess refractive index has relatively high negative values in comparison to binary system (DC+PE) specially at mid values of mole fraction range.it is cleary visible that values of deviations of refractive indices are very small for the whole mole fraction range.

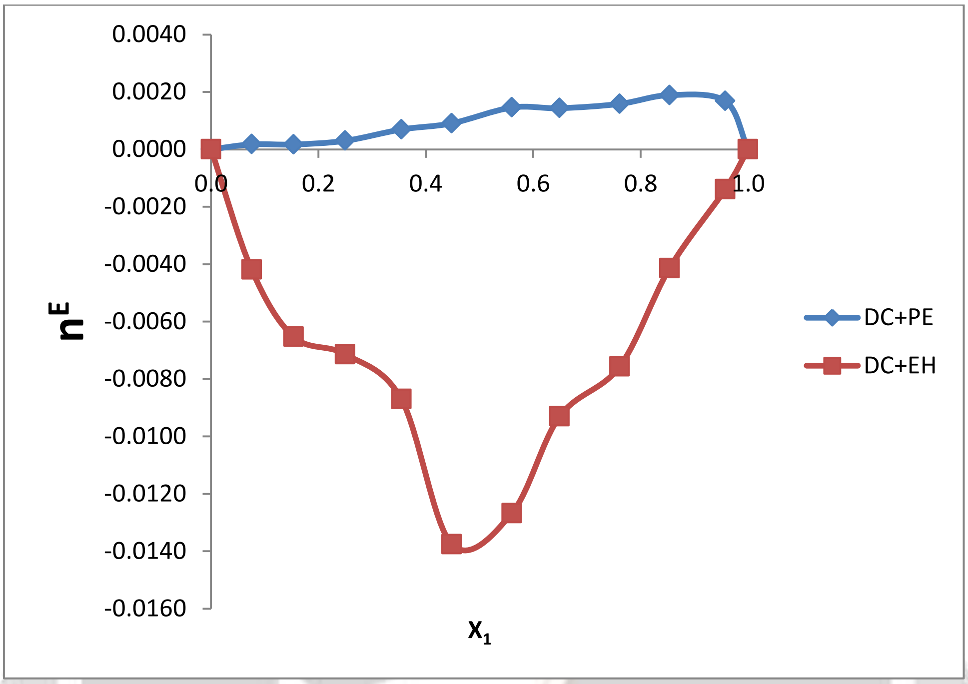

Figure-3 Excess refractive index vs. mole fraction for mixtures of (DC+PE) and (DC+EH) at 298K.

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 (DC+PE) at temperature 298K as a function of the mole fraction x_1 of DC.

X_1	ρ	n_m	V^E	R^E	n^E
0.0000	0.8829	1.3821	0.0000	0.0000	0.0000
0.0756	0.8731	1.3817	0.5873	-0.0879	0.0002
0.1539	0.8629	1.3811	1.1459	-0.1736	0.0002
0.2498	0.8527	1.3805	1.4596	-0.3133	0.0003
0.3543	0.8428	1.3801	1.5581	-0.4483	0.0007
0.4482	0.8331	1.3796	1.6630	-0.5155	0.0009
0.5601	0.8233	1.3793	1.4747	-0.5715	0.0015
0.6491	0.8125	1.3786	1.5869	-0.5088	0.0014
0.7609	0.8023	1.3779	1.2315	-0.4338	0.0016
0.8537	0.7934	1.3775	0.8907	-0.2764	0.0019
0.9577	0.7829	1.3765	0.4556	-0.0163	0.0017
1.0000	0.7811	1.3745	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 (DC+EH) at temperature 298K as a function of the mole fraction x_1 of DC.

X_1	ρ	n_m	V^E	R^E	n^E
0.0000	1.0278	1.4104	0.0000	0.0000	0.0000
0.0755	1.0035	1.4035	1.2856	-0.2440	-0.0042
0.1328	0.9855	1.3991	2.1588	-0.3774	-0.0065
0.2497	0.9536	1.3943	3.2346	-0.4986	-0.0071
0.3622	0.9201	1.3887	4.3704	-0.5510	-0.0087
0.4219	0.8955	1.3815	5.6693	-0.6121	-0.0138
0.5467	0.8711	1.3781	5.0261	-0.7542	-0.0127
0.6545	0.8462	1.3776	4.6478	-0.5856	-0.0093
0.7391	0.8275	1.3763	4.0696	-0.4801	-0.0076
0.8456	0.8031	1.3759	3.1828	-0.2031	-0.0041
0.9529	0.7845	1.3748	1.3611	-0.0166	-0.0014
1.0000	0.7811	1.3745	0.0000	0.0000	0.0000

CONCLUSIONS:

From above discussion it may be concluded that organic liquid mixtures taken in present study clearly shows that both systems have positive values for excess molar volume. But for one system it is small while high for other. Both systems have small negative values for excess molar refraction. Hence it may be said that these systems exhibits complex mixing behaviour and molecular interactions between components of organic liquid mixtures.

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