Molecular Interaction Study Through Thermophysical Properties For Some Binary Liquid Systems

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Abstract- *Refractive index and density have been measured for binary mixtures of o-dichlorbenzol with ethyl ethanoate and n-pentyl ethanoate 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.

I. INTRODUCTION

Study of thermophysical properties of organic liquids and their mixtures provide very important and deep knowledge about the molecular interactions between the molecules of liquid mixture.it also provides the information about rearrangements of molecules in a liquid mixture. Organic liquid mixture in comparison to pure organic liquids provides very valuable information about the molecular interactions, molecular structure etc. and for this reason study of thermophysical properties of liquid mixtures finds its application in various scientific and industrial applications [1-5]. The investigation of molecular interactions in different types of liquid mixtures with varying temperatures and compositions helps to predict the behavior of molecules after mixing very clearly. After mixing of pure components to prepare a liquid mixture various properties of pure component becomes changed and are considerably different from the original ones. Besides this some other properties viz. association and dissociation, complex formation etc. cannot be studied with the help of pure organic liquids alone [6-10]. Physicochemical properties of liquids along with their binary and ternary mixtures viz. Refractive Index, Viscosity, Surface Tension, Density etc. provides deep insight about the pure liquids and their mixtures. They provide very important information about molecular interactions, molecular structure, molecular orientations etc. For liquid mixtures, this forms very valuable database for the scientific and industrial applications. As far as ideal mixture is concerned it is known that their parameters should follow already settled well defined rules. But as per the category of mixtures it is seen that standard model of ideality declines according to the system. Thus idea of excess parameters constitutes new scale of ideality for these organic liquid mixtures. Thus deviation from ideality may be attributed by excess parameters. Number of workers suggests that occurrence of complex formation can be successfully explained by excess parameters as it represents the difference between partial molar property of a component in a mixture and that of pure components. Excess parameters viz. excess molar volume, excess molar refraction; excess refractive index etc. in combination with above physicochemical properties gives very important and deep knowledge about the interactions between molecules in organic liquid mixtures [11-15]. This type of study has many advantages. Firstly it may be considered as indirect but relatively convenient way to find out the nature and possibilities of interactions at microscopic level between like and unlike molecules of organic liquid mixtures. Secondly, with the help of this type of study we can set up experimental background to constitute, alter and investigate about the theories, models for the prediction of various properties of organic liquid mixtures. Lot of workers has made an attempt for this type of investigation. Excess enthalpy, adiabatic compressibility, intermolecular free length, internal pressure etc. are some other excess parameters which can also give very valuable information about organic liquids and their binary and ternary mixtures. Many workers performed such studies to explore about the molecular interactions, molecular structure, molecular rearrangements etc. in pure organic liquids and organic liquid mixtures. Number of methods and techniques are used to investigate about these properties of organic liquids and their binary and ternary mixtures. Some examples of these methods and techniques are Viscometric, Refractometric, Ultrasonic, Dielectric, X-ray, Vapour Pressure, FTIR, and NMR [16-22]. Out of these methods and techniques refractometric viscometric and ultrasonic techniques are extensively used by many workers as these methods and techniques requires comparatively low cost experimental setup but at the same time provides very prominent results. In present study we have used refractometric study to investigate about the molecular interactions, molecular structure and their rearrangements in organic liquid mixture. Index of refraction i.e. refractive index is a very important property of optical medium.it can provide very valuable information about liquids and their 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. Medium that have higher refractive index the speed of light is accordingly low in that medium. This is because of existing molecular interactions inside that medium and also due to the effect of these interactions with light. As we increase the temperature of medium refractive index becomes decreases, this clearly indicates about the changes at molecular level and thus molecular interactions accordingly affected. In this way refractive index is very deeply connected with the internal structure of medium and thus it can provide very valuable information about molecular interactions of liquid and their mixtures. Organic spices selected in this study are o-dichlorbenzol (OD), ethyl ethanoate (EE) and n-pentyl ethanoate (PE). OD is a very versatile organic liquid which is used in many industrial and scientific applications as solvent. It is used as insecticide, as chemical for synthesis of agrochemicals. EE is an ester which is highly miscible with almost all organic liquids. It is comparatively very low cost and low toxic organic liquid. On account of these advantages it finds huge application as solvent in scientific and industrial applications. It is also used in chemical industry e.g. in glues, nail polish remover etc. PE is also used as a solvent for number of natural and synthetic resins. It is effectively used in coating and painting industry. Due to its high extracting ability it is used in production of penicillin. It is also used as cleaners. Thus all the organic liquids taken in this study are very useful in many scientific, chemical and industrial applications [23-31]. To investigate about molecular interactions we have performed Refractometric and Excess parametric study for the binary mixtures of above mentioned organic liquids (OD+EE) and (OD+PE) over the whole mole fraction range of OD at 298K temperature.

II. EXPERIMENTAL

For the present work we have taken samples of selected organic spices that are of AR grade. They are purified by standard methods as given in literature [32-33]. To reduce the water content we have taken samples in dark bottles over 0.4nm molecular sieves and degassed with the help of vacuum pump. Purities of pure components of mixture was investigate with the help of Chromatographic method, and it is found that purities of pure components of liquid mixture were better than 0.995.Measurements were taken just after preparation of each component. Specially designed glass air tight ampoules were used to contain binary mixture of organic liquids and then weighed in single pan balance which has the accuracy of 0.0001gm. Evaporation losses of solvent were checked with the help of repeated measurements. Mole fraction was determined within the accuracy of ±0.0001.To find out the experimental values of refractive index of pure organic liquids and their binary mixtures; we have used Abbe refractometer in the present study. Before each use, calibration of Abbe refractometer was done using doubly distilled water and scale was checked before each measurement using test piece. Refractive indices measured in this study are accurate within the accuracy limit of ±0.0001.To inject the pure components and their binary mixture into the prism assembly of refractometer, we have used plastic syringe. An average of triplicate measurements was taken as final reading. For the density measurement we have used bicapillary pycnometer having bulb volume of $15cm^3$, and internal diameter of capillary of 1mm. Density measurements were accurate to ± $0.00001 gm\ cm^{-3}$ .Calibration of pycnometer was done with doubly 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.

III. 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 (OD+EE) and (OD+PE) 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 (OD+EE) and (OD+PE) 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 $\phi_1 = x_1V_1 / \sum x_iV_i$ and $\phi_2 = x_2 V_2 / \sum x_i V_i$

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 (OD+EE) and (OD+PE) 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 binary system (OD+EE) and V^E have negative values for binary systems (OD+PE) over the entire range of mixture composition. Positive values of V^E may reflects that there exists lesser intermolecular interactions for the binary systems (OD+EE) while negative values of (OD+PE) may be attributed for comparatively strong molecular interactions between molecules of organic liquid mixture.

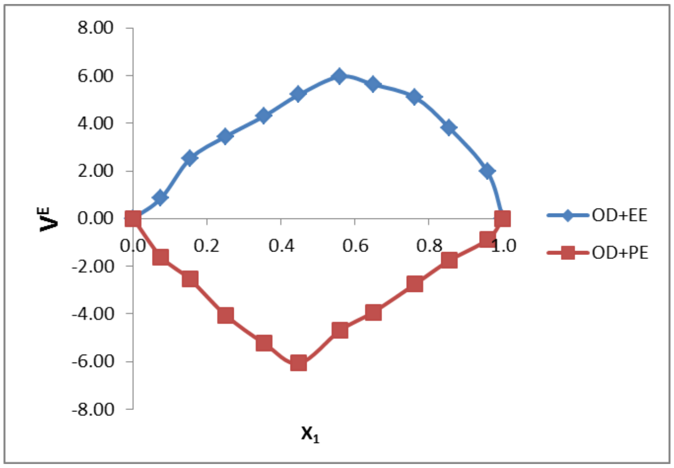

Figure-1 Excess molar volume vs. mole fraction for binary mixtures (OD+EE) and (OD+PE) at 298K.

Maxima for binary system (OD+EE) occurs for mole fraction value of about 0.5 while maxima for binary system (OD+PE) occurs for mole fraction value of about 0.4.thus it may be considered that both maxima occurs in mid value of mole fraction range.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 (OD+EE) and (OD+PE) as a function of mole fraction (x_1) of OD at 298K temperature is presented in figure-2.

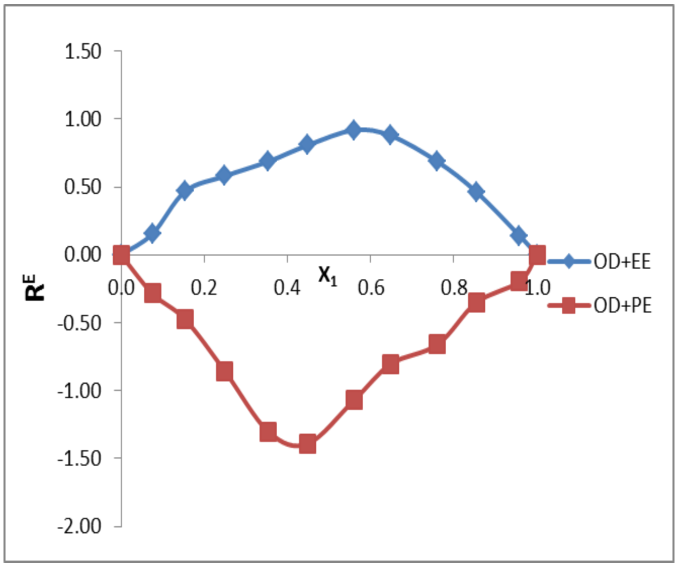

Figure-2 Excess molar refraction vs. mole fraction for binary mixtures (OD+EE) and (OD+PE) at 298K.

It shows that excess molar refraction R^E have positive values for binary system (OD+EE) and R^E have negative values for binary system (OD+PE) over the entire range of mixture composition for temperature 298K. . Maxima for binary system (OD+EE) occurs for mole fraction value of about 0.5 while maxima for binary system (OD+PE) occurs for mole fraction value of about 0.4.thus it may be considered that both maxima occurs in mid value of mole fraction range. This is exactly same as seen for excess molar values for both the liquid mixtures as given above.

The results of excess refractive index n^E for both the binary systems (OD+EE) and (OD+PE) as a function of mole fraction (x_1) of OD 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 (OD+EE) is positive for mole fraction range up to about 0.5 while for further values of mole fraction excess refractive index for binary system (OD+EE) becomes negative. On the other hand for the binary system (OD+PE) value of excess refractive index has negative value for the entire range of mole fraction values. It is seen that for binary system (OD+PE) excess refractive index values exhibits some complex behaviour for the mole fraction values between 0.3 to 0.6.for whole mole fraction range, it is also observed that deviation of refractive indices are very small.

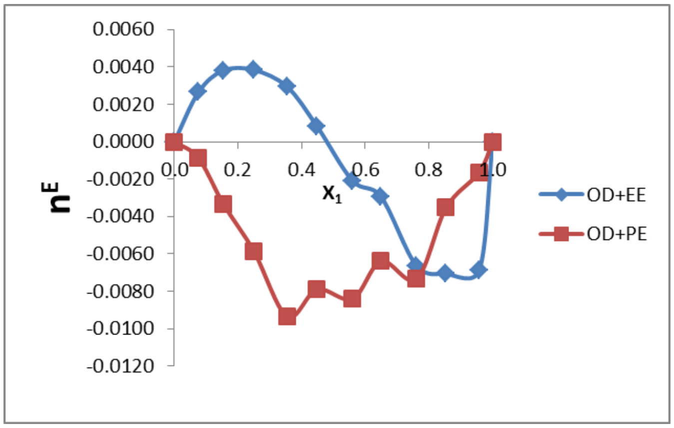

Figure-3 Excess refractive index vs. mole fraction for mixtures of (OD+EE) and (OD+PE) at 298K

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

X_1	ρ	n_m	V^E	R^E	n^E
0.0000	0.8947	1.3715	0.0000	0.0000	0.0000
0.0756	0.9216	1.3876	0.8603	0.1552	0.0026
0.1539	0.9414	1.4027	2.5107	0.4673	0.0038
0.2498	0.9742	1.4198	3.4420	0.5803	0.0038
0.3543	1.0098	1.4375	4.3001	0.6876	0.0029
0.4482	1.0393	1.4521	5.1960	0.8071	0.0008
0.5601	1.0758	1.4691	5.9608	0.9187	-0.0021
0.6491	1.1129	1.4841	5.6272	0.8769	-0.0029
0.7609	1.1598	1.5003	5.0921	0.6855	-0.0066
0.8537	1.2067	1.5164	3.8208	0.4642	-0.0071
0.9577	1.2639	1.5351	1.9681	0.1410	-0.0069
1.0000	1.3011	1.5495	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 (OD+PE)) at temperature 298K as a function of the mole fraction x_1 of OD.

X_1	ρ	n_m	V^E	R^E	n^E
0.0000	0.8759	1.3998	0.0000	0.0000	0.0000
0.0573	0.9046	1.4075	-1.6074	-0.2858	-0.0009
0.1498	0.9429	1.4189	-2.5489	-0.4752	-0.0033
0.2529	0.9917	1.4318	-4.0506	-0.8578	-0.0059
0.3503	1.0395	1.4429	-5.2364	-1.3032	-0.0093
0.4489	1.0883	1.4591	-6.0678	-1.3916	-0.0079
0.5611	1.1265	1.4754	-4.6850	-1.0702	-0.0084
0.6472	1.1598	1.4903	-3.9260	-0.8021	-0.0064
0.7497	1.1985	1.5047	-2.7617	-0.6602	-0.0073
0.8559	1.2426	1.5244	-1.7674	-0.3518	-0.0035
0.9428	1.2795	1.5393	-0.8833	-0.1968	-0.0016
1.0000	1.3011	1.5495	0.0000	0.0000	0.0000

IV. CONCLUSION

From the above discussion it is clear that we have both positive and negative values for excess molar volume, excess molar refraction and excess refractive index for both the binary systems. Above study delivers considerable focus on molecular interactions for both the organic liquid mixture. It may be said that both systems exhibits complex mixing behaviour and molecular interactions between components of organic liquid mixtures.

REFERENCES

[1] Pal, H. Kumar, Fluid Phase Equilib., 181, 17, (2001).
[2] Sastry N V, Patel S R and Prasad D H L, Thermochemica Acta, 359, 169, (2000).
[3] Ali, A.; Hyder, S.; Nain, A.K. J. Mol. Liq., 79, 89,(1999).
[4] Ali, A.K. Nain, V.K. Sharma, S. Ahmad, Ind. J. Phys. 75B, 519, (2001).
[5] Pal, H. Kumar, Ind. J. Phys. 75B, 419, (2001).

[6] M. Gupta, I. Vibhu, J.P. Shukla, J. Phys. Chem. Liq. 41, 575, (2003).
[7] Pal, H. Kumar, Fluid Phase Equilib. 181, 17, (2001).
[8] T.M. Letcher, G.G. Redhi, Fluid Phase Equilib. 198, 257, (2002).
[9] Francesconi, R.; Comelli, F.; Castellari, C. J. Chem. Eng. Data., 45, 544, (2000).
[10] Kumar M,Akbar S IJAR,Vol-1,4,211-213 (2012).
[11] Vural, U.S.; Yuruk, H.; Muradoglu, V. Rus. J. Phys. Chem., 77, 1091, (2003).
[12] Nayak, J.N., Aralaguppi, M.I., Toti, U.S., Amina Bhavi, T.M., J.Chem. Eng. Data. 48, 1483-1488, (2003).
[13] S. Singh, S. Parveen, D. Shukla, M. Gupta and J.P. Shukla Acta Physica Polonica A No. 6, Vol. 111, (2007).
[14] Vural, U.S.; Muradoglu, V.; Yuruk, H. Rus. J. Phys. Chem.,78, 33, (2004).
[15] Kumar M,Akbar S IJAR,Vol-1,5,197-199 (2012).
[16] Aralaguppi, M.I., Jadar, C.V., Aminabhavi, T.M., J. Chem.. Eng. Data. 44, 446-450, (1999).
[17] Mehra R and Israni R Indian J. Pure Appl. Phys. 38, 81,(2000).
[18] M. Gupta, I. Vibhu, J.P. Shukla, Fluid Phase Equilib. 244, 26, (2006).
[19] T.M. Aminabhavi, J. Chem. Eng. Data 29, 54, (1984).
[20] Sastry N V, and Dave P N, Thermochemica Acta., 286, 119,(1996).
[21] Luo B, Hamam B E M, Benson G C and BC-Y-Lu, J Chem Thermodyn.,18,1043, (1986).
[22] Vural, U.S. Russ. J. Phys. Chem., 79, 1096, (2005.)
[23] Sharma, S., Patel, P.B., Patel, R.S., Vora, J.J., E.J. Chem. 4, 343-349, (2007).
[24] Mehra, R., Proc. Indian Acad. Sci. 115, 147-1547, (2003).
[25] Araguppi, M.I., Jadar, C.V., Aminabhavi, T.M., J.Chem. Eng. Data. 44, 441-445, (1999).
[26] Aminabhavi, T. M., & Banerjee, K., J. Chem. Eng. Data., 43, 514-518, (1998).
[27] Pal, A., Kumar, H., Maan, R. and Sharma, K., J. of Solution Chemistry, 42(10),(2013).
[28] Nandhibatla V. Sastry, Sunil R. Patel, Saurabh S. Soni, J. Mol. Liquids, 183, 102 – 112. (I. F. 1.649), (57).
[29] Pal Amalendu, Kumar Harsh, Maan Ritu, Sharma Harish Kumar: J. Chem. Eng. Data , 58, 225, (2013).
[30] Pal Amalendu, Kumar Harsh, Maan Ritu, Sharma Harish Kumar: J. Chem. Eng. Data 2013, 58, 3190, (2013).
[31] Aralaguppi, M.I., Jadar, C.V., Aminabhavi, T.M., J. Chem. Eng. Data. 44, 435-440 (1990).
[32] A.I.Vogel; Text Book of Practical Organic Chemistry 5th ed. Longman Green, London,(2004).
[33] J.A.Riddick, W.B.Bunger, T.Sakano; Organic Solvents: Physical Properties and Methods of Purification, Wiley-Interscience, New York, (1986).
[34] Kim, E.S.; Marsh, K.N. J. Chem. Eng. Data, 33, 288, (1988).
[35] Dominguez, M.; Pardo, J.; Lopez, M.C.; Royo, F.M.; Urieta, J.S. Fluid Phase Equilib. , 124, 147, (1996).
[36] C.S.M. Pereira, V.M.T.M. Silva, A.E. Rodrigues, a review, Green Chem. 13 2658–2671,(2011).
[37] C.T. Bowmer, R.N. Hooftman, A.O. Hanstveit, P.W.M. Venderbosch, N.V. Hoeven, Chemosphere 37,1317–1333,(1998).
[38] M. Reisch, Solvent users look to replace NMP, Chem. Eng. News 86, 32,(2008).
[39] Sheu, Y.;Hsium. C.,J. Chem. Eng. Data., 50, 1706-1710,(2005).
[40] Maukonda. S.; Kumar. G.P.; Babu. Ch. P, Int. Lett. Chem, Phy and Astronomy, 40,17-23,(2014.)
[41] Pavai. R.; penuka. S.; Balu.L.; Vasanthani. V. J. Exp. Sci.,1(6), 21-24, (2010).
[42] Rathnam. M.; Mohite. S.; Kumar. M.,J.Serb. Chem.Soc.,77(4), 507-521, (2012).