



## Density and refractive index study on mixing properties of binary mixtures of 1,2-ethanediol with aliphatic alcohols at 298.15 K

Balasaheb B.Arbad\*, Madhuri J.Bawa, Shama B.Lomte, Machhindra K.Lande

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University,

Aurangabad-431004, Maharashtra, (INDIA)

E-mail : abr\_chem@yahoo.co.in

Received: 23<sup>rd</sup> March, 2009 ; Accepted: 28<sup>th</sup> March, 2009

### ABSTRACT

Density and refractive index have been experimentally determined for binary liquid mixtures of 1,2-ethanediol with aliphatic alcohols such as methanol, ethanol, 1-propanol and 1-butanol over the entire mole fraction range at 298.15K. Using the experimental values of densities and refractive indices, the excess molar volumes and refractive index deviations were calculated. The results were fitted by Redlich-Kister polynomial equation. The results were discussed in terms of intermolecular interaction between the mixing components. © 2009 Trade Science Inc. - INDIA

### KEYWORDS

Density;  
Refractive index;  
Excess properties;  
1,2-Ethanediol;  
Aliphatic alcohols.

### INTRODUCTION

Thermodynamic and transport properties provides important information for the design of industrial processes, to improve our understanding of the molecular interaction existing in the liquid mixtures, and to test the predictive capability of the models and methods developed to predict these properties<sup>[1,2]</sup>. Measurement of some of the bulk properties like density, refractive index have been widely used in the field of interactions and structural aspect evaluation studies<sup>[3]</sup>. In other word, these bulk properties have been adequately employed in understanding the nature of molecular systems and physicochemical behavior in liquid mixtures<sup>[4,5]</sup>. In the foregoing study, we report excess molar volumes ( $V^E$ ) and deviations in refractive index ( $\Delta n_p$ ) for binary liquid mixtures of 1,2-ethanediol with methanol, ethanol, 1-propanol and 1-butanol at 298.15K.

### EXPERIMENTAL

#### Materials

1,2-Ethanediol (S.D fine AR) was dried over anhydrous sodium sulphate<sup>[6]</sup> and Methanol, Ethanol, 1-Propanol, 1-Butanol (S.D.Fine AR) were purified by anhydrous calcium chloride<sup>[7]</sup>. All the liquids were filtered and distilled at atmospheric pressure, and stored over 4Å molecular sieves. The triple distilled liquids invariably were used. The purity of purified solvents was checked by comparing the measured densities and refractive indices with those reported in the literature. The measured values are included in TABLE 1 along with the literature values.

#### Measurements

The binary liquid mixtures were prepared by mixing known masses of pure liquids in airtight-stoppered

## Full Paper

bottles in order to minimize the evaporation losses. All measurements of mass were performed on a Mettler one-pan balance (E-METTLER, ZURICH), which allows reading up to fifth decimal digit, with a precision of  $\pm 0.05$  mg. The uncertainty in the mole fractions of the mixtures was estimated to be  $\pm 5 \times 10^{-5}$ .

Densities of pure components and their mixtures were measured using the single arm capillary pycnometer having a bulb volume of approximately  $5 \text{ cm}^3$  and a capillary bore with an internal diameter of 0.75 mm. The uncertainty in the density measurements was found to be  $\pm 3 \times 10^{-5} \text{ g.cm}^{-3}$ . The pycnometer was calibrated using double distilled water at 298.15 K

The refractometer was calibrated by means of a glass test piece of known refractive index supplied by the manufacturer. At a level of confidence of 99.7%, the uncertainty in the refractive index measurement was  $\pm 3 \times 10^{-4}$ . Calibration was performed by measuring the refractive indices of doubly distilled water, ethanol at defined temperature. The sample mixture was directly injected into the prism assembly of the instrument using an airtight hypodermic syringe, and an average of five measurements was taken for each mixture. For all the measurements, temperature was controlled by circulating the water through an ultra thermostat JULABO F-25 which has an accuracy  $\pm 0.02^\circ\text{C}$ .

**TABLE 1: Densities and refractive indices of pure components at 298.15 K**

Liquids	$\rho / \text{g.cm}^{-3}$		$n_D$	
	Exptl.	Lit.	Exptl.	Lit.
1,2-Ethanediol	1.09892	1.11000 [6]	1.4305	1.4310 [14]
Methanol	0.78634	0.78637 [5]	1.3265	1.3265 [5]
Ethanol	0.78496	0.78493 [5]	1.3629	1.3594 [5]
1-Propanol	0.79963	0.79960 [9]	1.3834	1.3843 [13]
1-Butanol	0.80572	0.80575 [9]	1.3972	1.3973 [13]

**TABLE 2: Measured density and refractive index values for 1,2-ethanediol + methanol, ethanol, 1-propanol and 1-butanol at 298.15 K.**

$x_1$	$\rho / (\text{g.cm}^{-3})$	$n_D$	$x_1$	$\rho / (\text{g.cm}^{-3})$	$n_D$	$x_1$	$\rho / (\text{g.cm}^{-3})$	$n_D$
0.0000	0.78634	1.3265	0.2560	0.87767	1.3982	0.6737	1.00671	1.4344
0.0356	0.80032	1.3424	0.3112	0.89619	1.4074	0.7704	1.03421	1.4348
0.0736	0.81444	1.3540	0.3711	0.91539	1.4160	0.8785	1.06479	1.4335
0.1143	0.82909	1.3669	0.4364	0.93587	1.4229	1.0000	1.09892	1.4305
0.1580	0.84451	1.3778	0.5080	0.95777	1.4284	-	-	-
0.2052	0.86078	1.3881	0.5867	0.98132	1.4320	-	-	-
<b>1,2-Ethanediol + Methanol</b>								
0.0000	0.78496	1.3629	0.3310	0.88001	1.4111	0.7480	1.01176	1.4255
0.0503	0.79916	1.3740	0.3937	0.89888	1.4154	0.8283	1.03873	1.4265
0.1025	0.81376	1.3834	0.4589	0.91893	1.4188	0.9122	1.06767	1.4282
0.1565	0.82889	1.3922	0.5268	0.94010	1.4214	1.0000	1.09892	1.4305
0.2125	0.84505	1.3995	0.5975	0.96255	1.4231	-	-	-
0.2707	0.86205	1.4058	0.6712	0.98639	1.4245	-	-	-
<b>1,2-Ethanediol + 1-Propanol</b>								
0.0000	0.79963	1.3834	0.3923	0.89301	1.4129	0.7948	1.01901	1.4249
0.0647	0.81357	1.3898	0.4586	0.91136	1.4156	0.8629	1.04417	1.4266
0.1296	0.82793	1.3961	0.5253	0.93071	1.4179	0.9313	1.07079	1.4285
0.1949	0.84301	1.4013	0.5922	0.95107	1.4200	1.0000	1.09892	1.4305
0.2604	0.85882	1.4058	0.6594	0.97247	1.4216	-	-	-
0.3262	0.87548	1.4097	0.7270	0.99504	1.4232	-	-	-
<b>1,2-Ethanediol + 1-Butanol</b>								
0.0000	0.80572	1.3972	0.3923	0.89887	1.3521	0.7948	1.02226	1.4101
0.0647	0.81953	1.3714	0.4586	0.91708	1.3597	0.8629	1.04658	1.4185
0.1296	0.83394	1.3563	0.5253	0.93613	1.3690	0.9313	1.07207	1.4251
0.1949	0.84907	1.3477	0.5922	0.95609	1.3803	1.0000	1.09892	1.4305
0.2604	0.86491	1.3448	0.6594	0.97711	1.3909	-	-	-
0.3262	0.88151	1.3467	0.7270	0.99909	1.4005	-	-	-

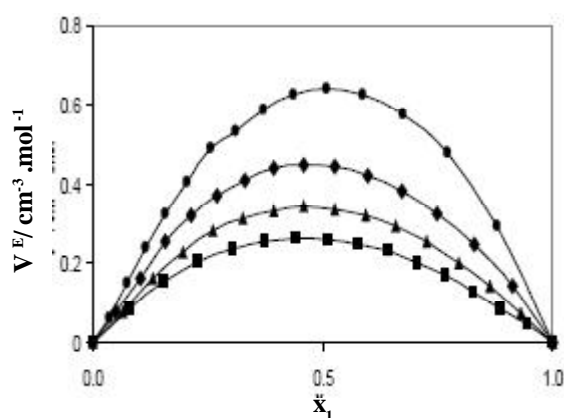
## RESULTS AND DISCUSSION

The experimentally determined values of densities ( $\rho$ ) and refractive indices ( $n_D$ ) for the binary liquid mixture of 1,2-Ethanediol with aliphatic alcohols at 298.15, are summarized in TABLE 2.

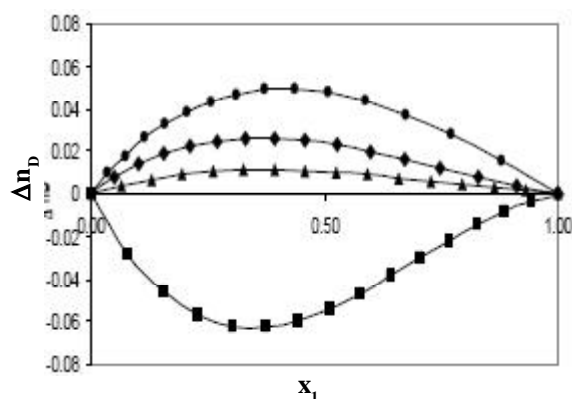
From the values of densities ( $\rho$ ), refractive indices

**TABLE 3: Coefficients,  $\alpha_i$  of eq. (4) and standard deviations,  $\sigma$  for the binary mixtures at 298.15 K**

Parameter	$\alpha_0$	$\alpha_1$	$\alpha_2$	$\sigma$
1,2-Ethanediol (1)+ Methanol (2)				
VE/cm <sup>3</sup> .mol <sup>-1</sup>	2.5719	0.1946	0.0029	0.0095
$\Delta n_D$	0.1955	-0.0796	2.7496	0.0008
1,2-Ethanediol (1) + Ethanol (2)				
VE/cm <sup>3</sup> .mol <sup>-1</sup>	1.4097	-0.0023	1.1088	0.1106
$\Delta n_D$	0.1007	-0.0765	0.0236	0.0007
1,2-Ethanediol(1)+1-Propanol (2)				
VE/cm <sup>3</sup> .mol <sup>-1</sup>	1.3727	-0.1692	-0.1090	0.0038
$\Delta n_D$	0.0407	-0.0256	-0.0019	0.0001
1,2-Ethanediol(1)+ 1-Butanol (2)				
VE/cm <sup>3</sup> .mol <sup>-1</sup>	1.0574	-0.1956	-0.0308	0.0016
$\Delta n_D$	-0.2013	0.1707	-0.0012	0.0003



**Figure 1: Variation of excess molar volume ( $V^E$ ) against mole fraction ( $x_1$ ) of 1,2-ethanediol at 298.15 K: (●) methanol, (◆) ethanol, (▲) 1-propanol, (■) 1-butanol**



**Figure 2: Variation of deviation in refractive index ( $\Delta n_D$ ) against mole fraction ( $x_1$ ) of 1,2-Ethanediol at 298.15 K: (●) Methanol, (◆) Ethanol, (▲) 1-Propanol, (■) 1-Butanol**

( $n_D$ ), the excess parameters such as excess molar volume ( $V^E$ ) and deviation in refractive index ( $\Delta n_D$ ) of all the mixtures at temperature 298.15 K has been calculated using following equations.

Excess molar volume<sup>[8]</sup> ( $V^E$ ) were calculated from the measured densities ( $\rho$ ) by using equation

$$V^E = ((x_1 M_1 + x_2 M_2) / \rho) - (x_1 V_1 + x_2 V_2) \quad (1)$$

Where  $\rho$  is the density of the mixture and  $M_1$ ,  $V_1$ ,  $x_1$  and  $M_2$ ,  $V_2$ ,  $x_2$  are the molecular mass, molar volumes and mole fractions of pure components 1 and 2 respectively.

The deviation in refractive index ( $\Delta n_D$ ) of binary mixtures were calculated<sup>[9]</sup> by using the simple additivity rule,

$$\Delta n_D = n_D - x_1 n_{D1} - x_2 n_{D2} \quad (2)$$

Where,  $n_D$ ,  $n_{D1}$  and  $n_{D2}$  are the refractive index of liquid mixture, pure components 1 and 2 respectively.  $x_1$  and  $x_2$  are mole fractions of pure components 1 and 2 respectively.

The calculated values of excess molar volumes ( $V^E$ ) and deviation in refractive indices ( $\Delta n_D$ ) were correlated by Redlich – Kister polynomial<sup>[10]</sup> as shown in Eq.:

$$\Delta Y = x_1 x_2 \sum a_i (x_1 - x_2)^i \quad (3)$$

The coefficients in equation (3) were estimated by the least squares fit method and the standard deviations were calculated by equation.

$$\sigma = [\sum (\Delta Y_{\text{Experimental}} - \Delta Y_{\text{Calculated}})^2 / (D - N)]^{0.5} \quad (4)$$

Where D and N are the number of data points and parameters, respectively.

Regression results for excess molar volumes and deviation in refractive indices of binary liquid mixture of 1,2-Ethanediol (1) and aliphatic alcohols as Methanol, Ethanol, 1-Propanol, and 1-Butanol (2) at 298.15 K are as shown in TABLE 3.

The graphical variation of  $V^E$  for the binary mixtures of 1,2-Ethanediol with Methanol, Ethanol, 1-Propanol and 1-Butanol with increasing mole fractions of 1,2-Ethanediol at 298.15 K is shown in figure 1. The values of excess molar volume are found to be positive for all the systems, where dispersion, induction and dipolar forces are operating, the values of excess molar volume are found to be positive, whereas the existence of specific interactions between the mixing components of the various binary systems tends to make excess molar volume negative<sup>[11]</sup>. Since, normally dispersive interaction between unlike molecules is weaker than those between like molecules, it is reasonable that they contribute positively<sup>[12]</sup> to  $V^E$ . In these systems the excess molar volume values decrease with increase in carbon atom of alcohol, which results solute-solvent interac-

## Full Paper

tion between mixing components.

Figure 2 shows the graphical variation of  $\Delta n_D$  for the binary mixtures of 1,2-Ethanediol with Methanol, Ethanol, 1-Propanol and 1-Butanol with increasing mole fractions of 1,2-Ethanediol at 298.15 K. In the present study, the values of  $\Delta n_D$  are found to be positive for the binary mixtures of 1,2-Ethanediol with Methanol, Ethanol and 1-Propanol but in the case of 1,2-Ethanediol + 1-Butanol,  $\Delta n_D$  values are found to be negative due to larger number of electron withdrawing group at 298.15 K temperatures, that means there is decrease in  $\Delta n_D$  values with increase in carbon atom of alcohols.

Hence in conclusion, we can say that even though some dispersion interaction is observed in case of all these binary mixtures or dominance of dispersion forces<sup>[13,14]</sup> is observed. Since, normally dispersive interaction between unlike molecules is weaker than those between like molecules.

### ACKNOWLEDGMENTS

The authors are thankful to Head, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad for providing necessary facilities.

### REFERENCES

- [1] J.L.Trenzado, J.S.Matos; J.Chem. Eng.Data., **46**, 974 (2001).
- [2] D.V.Jahagirdar, B.R.Arbad, S.R.Mirgane, M.K.Lande, A.G.Shankarwar; J.Mol.Liq., **75**, 33 (1998).
- [3] J.N.Nayak, M.I.Aralaguppi, T.M.Aminabhavi; J.Chem.Eng.Data., **48**, 152 (2003).
- [4] M.Domingues, S.Radriguez, M.C.Lopez, F.M.Royo, J.S.Urieta; J.Chem.Eng.Data., **48**, 1037 (2003).
- [5] L.Albuquerque, C.Ventura, R.Goncalves; J.Chem.Eng.Data., **41**, 685 (1998).
- [6] A.I.Vogel; 'Text Book of Practical Organic Chemistry', 5<sup>th</sup> Ed., John-Wiley and Sons; New York, (1989).
- [7] J.A.Riddick, W.B.Bunger, K.Sakano; 'Organic Solvents Techniques of Chemistry', 4<sup>th</sup> Ed., Wiley; New York, **74**, 434 (1986).
- [8] S.Chen, Q.Lei, W.Fang; J.Chem.Eng.Data., **47**, 811 (2002).
- [9] V.K.Rattan, S.Singh, B.P.Sethi; J.Chem.Eng.Data., **49**, 1074 (2004).
- [10] O.Redlich, A.T.Kister; Ind.Eng.Chem., **40**, 345 (1948).
- [11] J.M.Aminabhavi, V.B.Patil; J.Chem.Eng.Data., **43**, 504 (2002).
- [12] N.N.Wankhede, M.K.lande, B.R.Arbad; J.Chem. Eng.Data., **50**, 969 (2005).
- [13] T.M.Aminabhavi, B.Gopalkrishna; J.Chem.Eng. Data., **40**, 462 (1995).
- [14] N.G.Tsierkezos, I.E.Molinon; J.Chem.Eng.Data., **43**, 989 (1998).
- [15] U.B.Kadam, A.P.Hiray, A.B.Sawant, M.Hasan; J.Chem.Eng Data., **51**, 60 (2006).