Excess Volume, Viscosity, Heat of Mixing and IR Spectral Studies of Some Binary Liquid Mixtures involving H-Bond

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Abstract

Densities and viscosities of binary liquid mixtures of 1,2-propanediol + cyclohexanone, 1,2-propanediol + benzaldehyde and 1,2-propandiol + methylbenzoate were measured at 308.15 K and 318.15 K over entire range of composition. From the density (ρ) and viscosity (η) data the excess thermodynamic properties, viz., the excess volume (V^E), molar volume (V), deviation in viscosity (Δη), interaction parameter (d) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) were calculated. The values of excess parameters namely V^E, Δη and ΔG^{*E} were fitted to Redlich Kister type polynomial equation. Further heat of mixing and IR spectra were studied at equimolar concentration. From these results, the nature of interaction has been discussed in terms of intermolecular interaction between the mixing components.

Key words: Excess volume, Deviation in viscosity, Excess Gibbs free energy of activation of viscous flow. Heat of mixing and IR-Study.

INTRODUCTION

Physico-chemical and thermodynamic investigations play an important role in helping to understand the nature and extent of patterns of molecular aggregation that exists in binary liquid mixtures and their sensitivities to variation in composition and molecular structure of pure components [1]. A full understanding of thermodynamic and transport properties of binary liquid mixtures is essential in many chemical engineering processes such as separation process, design calculation, heat transfer, mass transfer, fluid flow and so forth [2].

The present work is focused on the study of molecular interactions in binary liquid mixtures of 1,2-propanediol + cyclohexanone, 1,2-propanediol + benzaldehyde and 1,2-propanediol + methylbenzoate and reported experimental data such as density (ρ) and viscosity (η) at 308.15 K and 318.15 K over the whole composition range. From the experimental density and viscosity data, the values of excess volume (V^E), deviation in viscosity (Δη), molar volume (V), interaction parameter (d) and excess Gibbs free energy of viscous flow (ΔG^{*E}) were calculated respectively.

1,2-propanediol is self associated component through intermolecular and intramolecular hydrogen bonding and the dipole moment value is μ = 2.27 D.

Cyclohexanone exhibits weak dipole-dipole interaction in pure state and dipole moment value is μ = 3.01 D. Benzaldehyde and methyl benzoate are polar, non-associated in solution, flavour components and the dipole moment values are μ = 2.89 D, μ = 1.94 D and good hydrogen bonding acceptors. A survey of literature has shown that no experimental physico-chemical studies for the above binary liquid mixtures were reported earlier.

EXPERIMENTAL METHODS

The chemicals used in the present study are analytical grade (Merck) and further purified by standard methods [3,4]. Before use, the chemicals were dried by suitable drying agents to remove the water content, if any. The mixtures were prepared by knowing mass and were kept in special air tight glass stoppered conical type bottles to avoid evaporation. The weighing measurements were performed on a Shimasdzu Auy 220 Japan electronic digital balance with precision of ± 0.0001 g.

The density of pure liquids and their liquid mixtures were measured by using special type specific gravity bottle of 10 ml capacity with an accuracy ± 0.0001 g. The specific gravity bottle containing solution was immersed in a constant temperature water bath (Guna company) measured at 308.15 and 318.15 K. Each reported values are the average of at least three measurements.

The viscosity of pure liquids and their liquid mixtures were measured by using in Ostwald viscometer of 10 ml capacity. The viscosities at temperature 308.15 and 318.15 K were measured. The time given to attain thermal equilibrium for the content of viscometer was 15 min. The time of flow was measured with an accurate stop watch which is capable of measuring time to within 0.01 s. Three sets of reading for the flow time were taken and the average values were taken for each pure liquids and liquid mixtures.

Heat of Mixing

Heat of mixing of binary liquid mixtures were measured with calorimeter (Dewar flask) at equimolar concentration.

IR study

IR spectra for pure liquids and equimolar liquid mixtures were recorded by Perkin Elmer FT-IR.

RESULTS AND DISCUSSION

Comparison of experimental density (ρ) and viscosity (η) values with literature values for pure 1,2-propanediol, cyclohexanone, benzaldehyde and methylbenzoate are presented in Table-1. There is a good agreement with literature values at 308.15 and 318.15 K temperature for both density (ρ) and viscosity (η).

The densities (ρ) and viscosities (η) of given binary mixtures at 308.15 K and 318.15 K are presented in Tables 2-7, which also include the values of excess thermodynamic function viz., Excess volume (V^E), deviation in viscosity (Δη), molar volume (V) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}). It can be seen that variation of density and viscosity with composition of binary mixture is non-linear which indication the presence of molecular interaction [20].

The excess volume of the given binary liquid mixtures was evaluated from the molar volumes of mixtures and that of its pure components V_1 and V_2 using the equation (1) [21].

$$V^E = \left(\frac{x_1M_1 + x_2M_2}{\rho_{mix}}\right) - \left(\frac{x_1M_1}{\rho_1}\right) - \left(\frac{x_2M_2}{\rho_2}\right) \quad \text{... (1)}$$

The molar volume (V) of mixture and their pure liquids components were calculated from the measured density (ρ_{mix}) and pure liquids (1and 2) using the following equation (2) [22].

$$V = \sum_{i=1}^{n} \frac{x_i m_i}{\rho} \quad \text{... (2)}$$

where x_1, x_2 are the molefraction of the individual components of binary liquid mixtures respectively, $V_1 = \frac{M_1}{\rho_1}$ and $V_2 = \frac{M_2}{\rho_2}$, M_1 and M_2 are the molecular weight of the components 1 and 2. ρ_1, ρ_2 and ρ densities of the pure components 1, 2 and of the binary mixtures.

Viscosities of binary liquid mixtures and their pure liquids were calculated by using the following equation (3) [23].

$$\eta = \left(At - \frac{B}{t}\right)\rho \quad \text{... (3)}$$

where A and B are characteristic constant, t-is the time flow, ρ- is the density.

The deviation in viscosity (Δη) of the binary liquid mixtures was calculated from the observed viscosity of mixtures (η_{mix}) and that of its pure components using the equation (4) [24].

$$\Delta\eta = \eta_{mix} - (x_1\eta_1 + x_2\eta_2) \quad \text{... (4)}$$

where η_{mix} is the viscosity of binary liquid mixtures and η_1 and η_2 are the viscosity of pure component 1 and 2, x_1 and x_2 are the mole fraction of the components 1 and 2.

Grunberg and Nissan [25] put forward logarithmic relation between viscosity of binary liquid mixtures and their pure components in equation (5).

$$\Delta \ln\eta_{mix} = x_1 \ln\eta_1 + x_2 \ln\eta_2 + x_1 x_2 d \quad \text{... (5)}$$

where d is interaction parameter regarded as a measure of strength of interaction between mixing component molecules.

Excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) values for the liquid mixtures were computed from the following equation (6) [26].

$$\Delta G^{*E} = RT[\ln(\eta_{mix} V) - (x_1 \ln(\eta_1 v_1) + x_2 \ln(\eta_2 v_2))] \quad \text{... (6)}$$

where R is gas constant, T = 308.15 K and 318.15 K.

Excess values of other parameter are calculated using the relation (7)

$$A^E = A_{exp} - A_{id} \quad \text{... (7)}$$

$A_{id} = \Sigma x_i A_i$, x_i and A_i are the mole fraction and parameters of the i^{th} component liquid.

All the calculated excess values were fitted to Redlich-Kister type polynomial equation (8).

$$A^E = x_1 x_2 [a + b(x_1 - x_2) + c(x_1 - x_2)] \quad \text{... (8)}$$

by the method of least square to derive the adjustable parameter a, b and c. From these a, b and c values, theoretical values for all the excess parameters were calculated using the following relation (9).

$$\sigma = \left[\left(\left(A^E_{\exp} - A^E_{cal} \right)^2 / (n - m) \right) \right]^{1/2} \quad \text{... (9)}$$

where n is the number of measurements and m is the number of adjustable parameters. The values of a, b, c and σ are given in the Table-8.

Table 1.1:

Comparison of density (ρ) and viscosity (η) values with literature values of pure liquids at 308.15 K and 318.15 K

Name of the Components	Temperature K	Density ρ/g cm^{-3}		Viscosity η/m Pa.s	
		Expt.	Lit.	Expt.	Lit.
1,2-propanediol	308.15	1.0256	1.0251 [5]	21.3250	25.2200 [6]
	318.15	1.0199	1.0180 [7]	12.7391	12.7800 [8]
Cyclohexanone	308.15	0.9290	0.9306 [9]	1.3140	1.6562 [10]
	318.15	0.9237	0.9225 [11]	1.0640	1.3700 [12]
Benzaldehyde	308.15	1.0353	1.0324 [13]	1.0387	1.2490 [14]
	318.15	1.0254	1.0266 [15]	0.9542	1.0234 [16]
Methyl benzoate	308.15	1.0698	1.0706 [17]	1.4628	1.5100 [18]
	318.15	1.0623	1.0612 [19]	1.2654	1.2818 [20]

Table 1.2:

Densities, Viscosities and Excess Properties of Binary Liquid Mixtures of 1,2-Propanediol (1) + Cyclohexanone (2) at 308.15 K

x_1	ρ ($g.cm^{-3}$)	V^E ($cm^3.mol^{-1}$)	η (mPa.s)	Δη (mPa.s)	Δlnη (mPa.s)	d	V ($cm^3.mol^{-1}$)	ΔG^{*E} ($kJ.\ mol^{-1}$)
0.0000	0.9290		1.3140				105.4898	
0.1015	0.9369	-0.0851	2.7793	-0.5658	0.4663	-5.0737	102.2288	1.2056
0.2030	0.9452	-0.1612	4.5808	-0.7954	0.6831	-3.6626	98.97688	1.7698
0.2900	0.9531	-0.2576	6.1230	-0.9942	0.7308	-3.4393	96.1583	1.8964
0.3905	0.9625	-0.3347	8.0197	-1.1086	0.7206	-3.6377	92.9366	1.8735
0.4949	0.9728	-0.4091	10.1218	-1.0956	0.6624	-4.2951	89.5956	1.7248
0.6010	0.9824	-0.3290	12.4745	-0.8661	0.5757	-5.5996	86.3559	1.5040
0.6800	0.9900	-0.2617	14.2855	-0.6360	0.4911	-7.3045	83.9514	1.2861
0.7804	0.9999	-0.1505	16.4953	-0.4352	0.3552	-11.4807	80.9211	0.9341
0.8916	1.0123	-0.0744	18.9065	-0.2493	0.1817	-25.5944	77.5179	0.4799
1.0000	1.0256		21.3250				74.2005	

Table 1.3:

Densities, Viscosities and Excess Properties of Binary Liquid Mixtures of 1,2-Propanediol (1) + Cyclohexanone (2) at 318.15 K

x_1	ρ ($g.cm^{-3}$)	V^E ($cm^3.mol^{-1}$)	η (mPa.s)	$\Delta\eta$ (mPa.s)	$\Delta\ln\eta$ (mPa.s)	d	V ($cm^3.mol^{-1}$)	ΔG^{*E} ($kJ.\ mol^{-1}$)
0.0000	0.9237		1.0640				106.0950	
0.1015	0.9318	-0.1081	2.0362	-0.2128	0.3971	-2.7322	102.7917	1.0611
0.2030	0.9403	-0.2099	3.0674	-0.3667	0.5548	-2.3776	99.4948	1.4866
0.2900	0.9481	-0.2984	4.0184	-0.4313	0.6089	-2.4071	96.6675	1.6344
0.3905	0.9574	-0.3704	4.9804	-0.6427	0.5740	-2.7284	93.4317	1.5457
0.4949	0.9678	-0.4525	6.0926	-0.7494	0.5164	-3.3562	90.0631	1.3933
0.6010	0.9772	-0.3610	7.5468	-0.5339	0.4670	-4.4597	86.8147	1.2643
0.6800	0.9847	-0.2853	8.6715	-0.3316	0.4098	-5.8833	84.4034	1.1121
0.7804	0.9947	-0.1905	9.9173	-0.2579	0.2948	-9.3730	81.3377	0.8035
0.8916	1.0070	-0.0977	11.3180	-0.1556	0.1508	-21.1181	77.9298	0.4130
1.0000	1.0199		12.7391				74.6151	

Table 1.4:

Densities, Viscosities and Excess Properties of Binary Liquid Mixtures of 1,2-Propanediol (1) + Benzaldehyde (2) at 308.15 K

x_1	ρ ($g.cm^{-3}$)	V^E ($cm^3.mol^{-1}$)	η (mPa.s)	$\Delta\eta$ (mPa.s)	$\Delta\ln\eta$ (mPa.s)	d	V ($cm^3.mol^{-1}$)	ΔG^{*E} ($kJ.\ mol^{-1}$)
0.0000	1.0353		1.0387				102.4824	
0.1025	1.0351	-0.0497	1.8548	-1.2632	0.2701	-3.1620	99.5338	0.7019
0.2103	1.0347	-0.0889	3.9582	-1.3439	0.7024	-2.6928	96.1690	1.8426
0.2945	1.0344	-0.1205	5.5969	-1.4161	0.7943	-2.7439	94.0329	2.0581
0.4005	1.0340	-0.1651	7.5720	-1.5914	0.7762	-3.1744	90.9903	2.0152
0.5049	1.0336	-0.2065	9.4232	-1.8581	0.6794	-4.0124	87.9964	1.7679
0.6048	1.0320	-0.1540	11.6619	-1.6459	0.5907	-5.3491	85.2235	1.5412
0.6934	1.0307	-0.1158	13.6639	-1.4413	0.4814	-7.4200	82.7559	1.2592
0.7925	1.0292	-0.0767	15.7714	-1.3442	0.3254	-12.0361	79.9923	0.8544
0.9016	1.0275	-0.0505	18.1002	-1.2287	0.1334	-28.2425	76.9329	0.3529
1.0000	1.0256		21.325				74.2005	

Table 1.5:

Densities, Viscosities and Excess Properties of Binary Liquid Mixtures of 1,2-Propanediol (1) + Benzaldehyde (2) at 318.15 K

x_1	ρ ($g.cm^{-3}$)	V^E ($cm^3.mol^{-1}$)	η (mPa.s)	Δη (mPa.s)	Δlnη (mPa.s)	d	V ($cm^3.mol^{-1}$)	ΔG^{*E} ($kJ.\ mol^{-1}$)
0.0000	1.0254		0.9542				103.4718	
0.1025	1.0257	-0.0692	1.5412	-0.6210	0.2138	-1.9454	100.4448	0.5757
0.2103	1.0256	-0.1076	2.6892	-0.7408	0.4910	-2.0212	97.0163	1.3433
0.2945	1.0257	-0.1491	3.5623	-0.8626	0.5541	-2.1773	94.8244	1.4894
0.4005	1.0257	-0.1914	4.7371	-0.9370	0.5644	-2.5722	91.7233	1.5204
0.5049	1.0258	-0.2339	5.8978	-1.0066	0.5130	-3.2723	88.6682	1.3851
0.6048	1.0247	-0.1871	7.1484	-0.9333	0.4464	-4.3946	85.8322	1.2094
0.6934	1.0237	-0.1385	8.3220	-0.8039	0.3688	-6.1132	83.3241	1.0023
0.7925	1.0226	-0.0993	9.5594	-0.7344	0.2506	-9.9468	80.5036	0.6843
0.9016	1.0216	-0.0757	10.9307	-0.6488	0.1019	-23.4170	77.3790	0.2807
1.0000	1.0199		12.7391				74.6151	

Table 1.6:

Densities, Viscosities and Excess Properties of Binary Liquid Mixtures of 1,2-Propanediol (1) + Methyl benzoate (2) at 308.15 K

x_1	ρ ($g.cm^{-3}$)	V^E ($cm^3.mol^{-1}$)	η (mPa.s)	$\Delta\eta$ (mPa.s)	$\Delta\ln\eta$ (mPa.s)	d	V ($cm^3.mol^{-1}$)	ΔG^{*E} ($kJ.\ mol^{-1}$)
0.0000	1.0698		1.4628				127.2200	
0.0987	1.0678	-0.0940	3.2905	0.0136	0.5843	-6.4812	109.1710	2.4827
0.2023	1.0658	-0.1848	5.5264	0.0455	0.7871	-4.0065	116.3094	2.0663
0.2946	1.0640	-0.2992	7.3794	0.0652	0.8289	-3.6302	111.3013	2.1882
0.4038	1.0611	-0.3813	9.5670	0.0838	0.7960	-3.8159	105.4294	2.1157
0.4950	1.0588	-0.4847	11.3895	0.0950	0.7260	-4.3949	100.4907	1.9394
0.6097	1.0531	-0.3978	13.6492	0.0764	0.5996	-5.8500	94.4962	1.6165
0.6895	1.0482	-0.2850	15.2136	0.0544	0.4939	-7.6525	90.5052	1.3330
0.8054	1.0409	-0.1920	17.4925	0.0327	0.3233	-13.3344	84.3261	0.8873
0.8937	1.0342	-0.0831	19.2333	0.0197	0.1816	-26.2543	79.7534	0.5033
1.0000	1.0256		21.3250				74.2005	

Table 1.7

Densities, Viscosities and Excess Properties of Binary Liquid Mixtures of 1,2-Propanediol (1) + Methyl benzoate (2) at 318.15 K

x_1	ρ ($g.cm^{-3}$)	V^E ($cm^3.mol^{-1}$)	η (mPa.s)	$\Delta\eta$ (mPa.s)	$\Delta\ln\eta$ (mPa.s)	d	V ($cm^3.mol^{-1}$)	ΔG^{*E} (kJ. mol^{-1})
0.0000	1.0623		1.2654				128.1182	
0.0987	1.0604	-0.0988	2.3953	0.1240	0.4337	-4.6870	109.9269	2.1670
0.2023	1.0589	-0.2228	3.8255	0.2390	0.6391	-3.0119	117.0717	1.7414
0.2946	1.0571	-0.3242	4.9909	0.3453	0.6919	-2.7988	112.0320	1.8965
0.4038	1.0551	-0.4813	6.3544	0.4559	0.6813	-3.0019	106.0324	1.8790
0.4950	1.0528	-0.5675	7.5585	0.6136	0.6442	-3.4918	101.0667	1.7844
0.6097	1.0471	-0.4566	8.7606	0.4997	0.5269	-4.7356	95.0409	1.4756
0.6895	1.0424	-0.3442	9.5322	0.3545	0.4268	-6.2558	91.0117	1.1975
0.8054	1.0352	-0.2338	10.7262	0.2199	0.2774	-10.9960	84.7931	0.7937
0.8937	1.0284	-0.1046	11.6284	0.1090	0.1543	-21.7486	80.1980	0.4469
1.0000	1.0199		12.7391				74.6151	

Table 1.8:

Adjustable parameters a, b and c for Redlich – Kister polynomial equation with the standard deviation (σ) for excess volume (V^E), deviation in viscosity (Δη) and excess Gibbs free energy of activation of flow (ΔG^{*E}) for binary mixtures of 1,2-propanediol+ cyclohexanone, 1,2-propanediol + benzaldehyde and 1,2-propanediol + methyl benzoate at temperature 308.15K and 318.15 K

Temperature	Parameters	a	b	c	σ
1,2-propanediol + Cyclohexanone					
308.15K	$V^E(cm^3mol^{-1})$	-1.4839	0.1358	1.3782	0.0197
	Δη(mPa.s)	-4.0999	2.2807	0.5427	0.0645
	ΔG^{*E} (KJ mol^{-1})	6.8825	-4.4890	3.5493	0.0514
318.15K	$V^E(cm^3mol^{-1})$	-1.6261	1.8799	1.1432	0.0172
	Δη(mPa.s)	-2.5170	0.7377	1.8252	0.0252
	ΔG^{*E} (KJ mol^{-1})	5.6931	-3.7644	3.6806	0.0540
1,2-propanediol + Benzaldehyde					
308.15K	$V^E(cm^3mol^{-1})$	-0.7068	0.0432	0.4973	0.0065
	Δη(mPa.s)	-6.3665	-0.1096	-7.6824	0.1161
	ΔG^{*E} (KJ mol^{-1})	7.5607	-4.4049	-0.2451	0.0070
318.15K	$V^E(cm^3mol^{-1})$	-0.8146	0.0293	0.3624	0.0045
	Δη(mPa.s)	-3.6806	0.0510	-3.5460	0.0533
	ΔG^{*E} (KJ mol^{-1})	5.7896	-2.9445	-0.2406	0.0053
1,2-propanediol + Methyl Benzoate					
308.15K	$V^E(cm^3mol^{-1})$	-1.7334	0.0243	1.4924	0.0189
	Δη(mPa.s)	0.3516	-0.0455	-0.3017	0.0039
	ΔG^{*E} (KJ mol^{-1})	7.1899	-7.4233	9.7251	0.1486
318.15K	$V^E(cm^3mol^{-1})$	-2.0524	-0.0254	1.7977	0.0230
	Δη(mPa.s)	2.1363	-0.1740	-1.8524	0.0234
	ΔG^{*E} (KJ mol^{-1})	6.5154	-6.1890	7.7381	0.1200

The excess volumes of binary mixtures of 1,2-propanediol + cyclohexanone, 1,2-propanediol + benzaldehyde and 1,2-propanediol+methylbenzoate were measured at 308.15 K and 318.15 K over the entire molefraction range. The experimental excess volumes are recorded in Tables 2-7 and plotted as a function of composition in Fig.1 and 2. The parameters a, b, and c are presented in Table 7 along with standard deviation σ.

The sign of V^E depends upon the contraction and expansion in volume of the liquids due to mixing. The factors that are mainly responsible for the expansion of excess volume, i.e., positive values of V^E are the following (i) breaking of the structure of one or both of the components in solution i.e., loss of dipolar association between the molecules. (ii) H – bond rupture and stretching of self associated molecules. (iii) The geometry of the molecular structures which does not favour the fitting of molecules of one component into other molecules of second component. (iv) Steric hindrance of the molecules. The negative values of V^E are due to the (i) association of molecules through the formation of hydrogen bond, i.e., strong specific interactions (ii) accommodation of molecules because of large difference in their molar volumes [27].

The V^E values are found to be negative for all the studied three binary mixtures over the entire composition range at 308.15 K and 318.15 K. Fig. 1 and 2 represent the variation of excess volume for cyclohexanone, benzaldehyde, methylbenzoate with molefraction of 1,2-propandiol respectively. The V^E versus x_1 curves are unsymmetrical. The negative V^E values indicate the existence of specific interactions like dipole-dipole and hydrogen bonded interaction between the unlike molecules of the mixing components.

When 1,2-propanediol is diluted with cyclohexanone, benzaldehyde or methyl benzoate gets completely soluble. This is due to the hydrogen bonding (OH ··· O = C) between the OH group of 1,2-propandiol molecule with C=O group of cyclohexanone, benzaldehyde and methylbenzoate molecules. Therefore negative V^E values are observed for all the three binary liquid mixtures.

Another negative contribution to V^E is due to geometrical fitting of smaller molecules into the voids created by larger molecules. Since the molar volumes of 1,2-propanediol, cyclohexanone, benzaldehyde and methyl benzoate are 74.2005 $cm^3.mol^{-1}$, 105.4898 $cm^3.mol^{-1}$, 102.4824 $cm^3.mol^{-1}$ and 127.2200 $cm^3.mol^{-1}$ at 308.15K. This implies that the molecules in the liquid mixture are more compact than that of corresponding pure liquids. The negative V^E values and strength of interactions in the present investigated systems follow the order:

1,2-propanediol + methylbenzoate > 1,2-propanediol + cyclohexanone > 1,2-propanediol + benzaldehyde

When temperature is increased from 308.15K to 318.15K the negative values become more negative, This may due to increase in kinetic energy and rate of association of dipolar interaction between the unlike molecules. Hence there is increase in attractive interaction with rise in temperature.

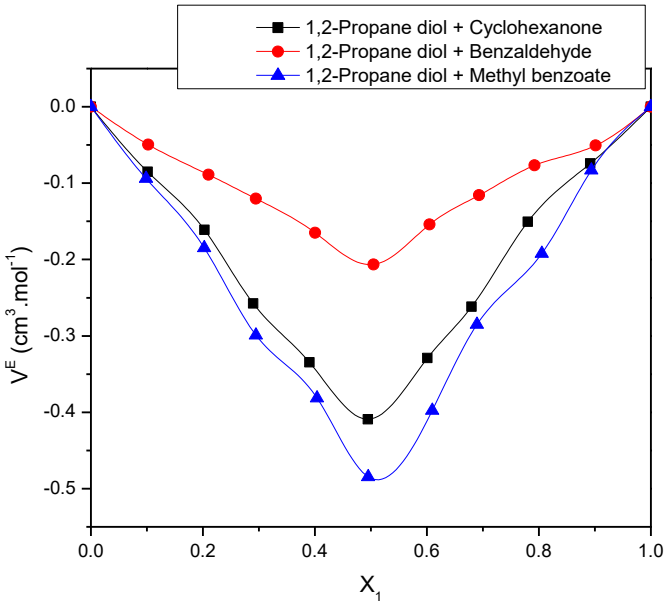

Fig. 1.1: Excess volume versus mole fraction curve for Binary Liquid Mixture of 1,2- Propanediol with Cyclohexanone, Benzaldehyde and Methyl benzoate at 308.15K.

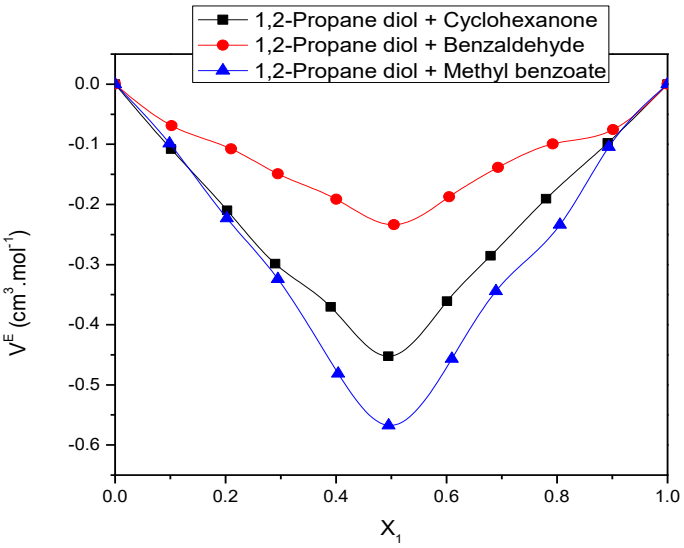

Fig.1.2: Excess volume versus mole fraction curve for Binary Liquid Mixture of 1,2-Propanediol with Cyclohexanone, Benzaldehyde and Methyl benzoate at 318.15K.

The calculated values of Δη, Δlnη and d are presented in Tables 2-7 over the entire range of composition at 308.15 K and 318.15 K. Negative values of Δη, d and positive values of Δlnη are observed over the whole concentration range at both temperatures except in the system of 1,2-propanediol + methylbenzoate for which Δη is positive. The variation Δη gives a qualitative estimation of strength of molecular interaction and viscous nature of liquid mixture. The negative values of Δη indicate the domination of weak forces and the positive values suggest the presence of strong interaction between the unlike molecules [28].

When temperature is increased, the Δη and d values are decreased. The strong positive deviation in viscosity (Δη) for 1,2-propanediol + methyl benzoate system would imply that (i) the mixture is more viscous than the other binary mixtures. The remaining two mixtures are less viscous and can flow more easily than that of corresponding pure liquids due to negative deviation of Δη and d.(ii) the strong specific interaction i.e., stronger hydrogen bonding interaction as incorporated by the large negative V^E values. Therefore, the viscous nature of liquid mixtures are in the following order:

1,2-propanediol + methylbenzoate > 1,2-propanediol + cyclohexanone > 1,2-propanediol + benzaldehyde

The variation of Δη in the present study suggest specific interactions such as new hydrogen bond between unlike molecules and dipole-dipole interactions are dominant.

The values of Gibbs free energy of activation of viscous flow (ΔG^{*E}) are recorded in Tables 2-7 at 308.15 K and 318.15 K for all the studied three binary liquid mixtures over entire molefraction range. ΔG^{*E} values are positive throughout whole concentration range at both temperatures. Negative values of ΔG^{*E} indicate the presence of weak physical forces such as dispersive forces in the system. On the other hand, positive values of it suggest strong specific interactions [29]. These positive ΔG^{*E} values are decreased when increasing temperature from 308.15 K to 318.15 K. The decrease in ΔG^{*E} with increase in temperature in all of the mixtures suggests that the presence of strong specific interaction like H-bond between unlike molecules.

Heat of Mixing

The heat of mixing value of the given binary systems at equimolar concentration were measured with a calorimeter. Generally, heat of mixing of binary and ternary liquid mixtures may be influenced by two factor such as (i) The absorption of heat [Endothermic] due to the dissociation of self associated liquids. (ii) The second factor is the liberation of heat [Exothermic] as result of hydrogen bonding formation between the component molecules [30].

Positive ΔH values are found out for the binary mixtures of 1,2-propanediol + cyclohexanone, 1,2-propanediol + benzaldehyde and 1,2-propanediol + methyl

benzoate shows endothermic effect which is due to absorption of heat during the process of mixing of liquids. The ΔH values are 1066.5 J.mol^{-1}, 932.3 J.mol^{-1} and 997.5 J.mol^{-1}. These less positive ΔH values reveal the presence of a specific interaction like hydrogen bond formation between the unlike molecules.

FT-IR Study

FT-IR spectra for pure 1,2-propanediol, cyclohexanone, benzaldehyde, methyl benzoate along with binary liquid mixture at equimolar concentration are recorded. The pure 1,2-propanediol exhibits -OH peak at 3339.8cm^{-1} and no OH peak is observed for cyclohexanone, benzaldehyde, methylbenzoate. Upon mixing, there is significant absorption frequency caused by stronger intermolecular H-bonding between the unlike molecules. It is clearly observed that for mixtures peaks appear at 3328.2 cm^{-1}, 3369.5 cm^{-1}, 3327.9 cm^{-1} and the spectrum is broad. These are clearly depicted in Figures 3-6. This may be due to formation of intermolecular hydrogen bond between OH group of 1,2-propanediol with C=O group of cyclohexanone, benzaldehyde and methyl benzoate. The bands that result from intermolecular hydrogen bonding appear at lower energies [31]. This strongly supports the conclusion drawn from V^E, Δη and ΔG^{*E} data.

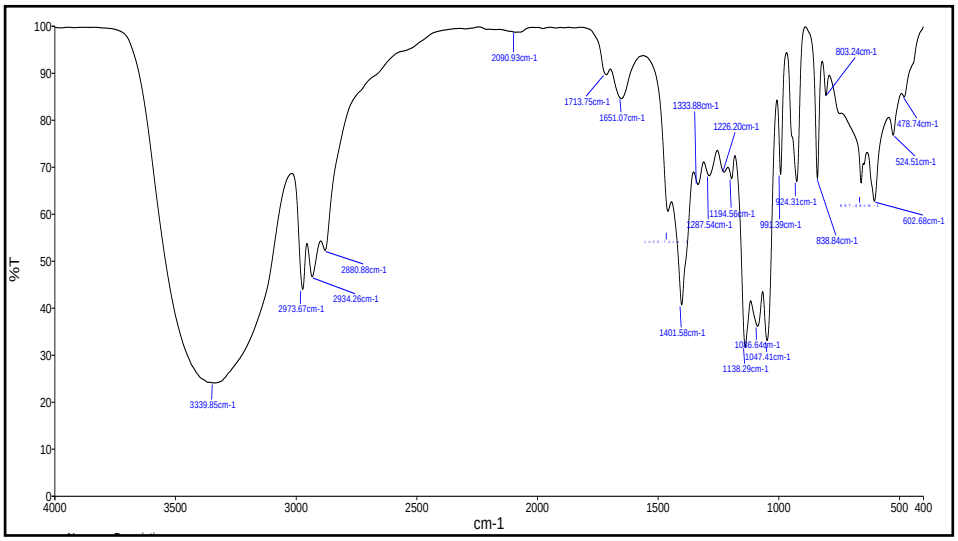

Fig. 3: FTIR – Spectra for pure 1,2-Propanediol Molecules

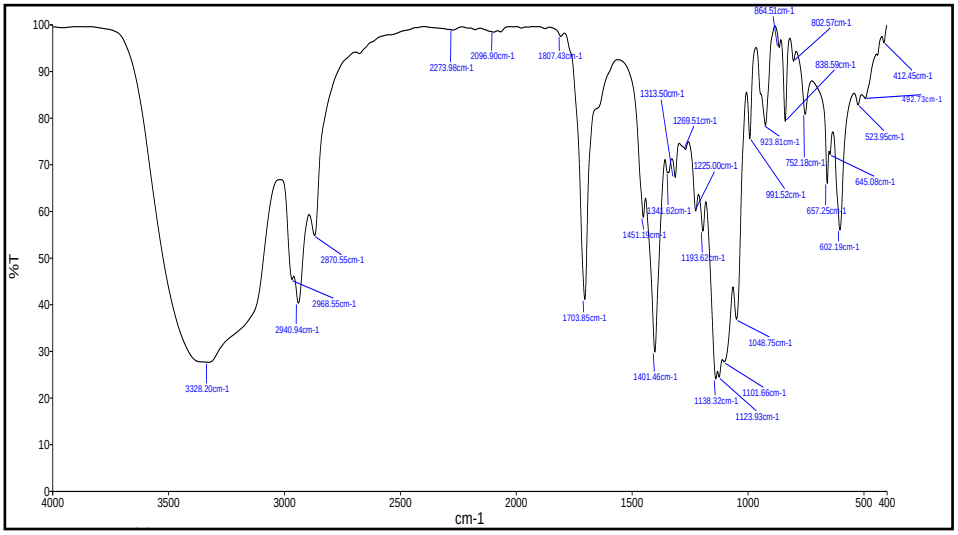

Fig. 4: FTIR – Spectra for Binary Liquid Mixtures of 1,2-Propanediol (1) + Cyclohexanone (2) at equimolar concentration.

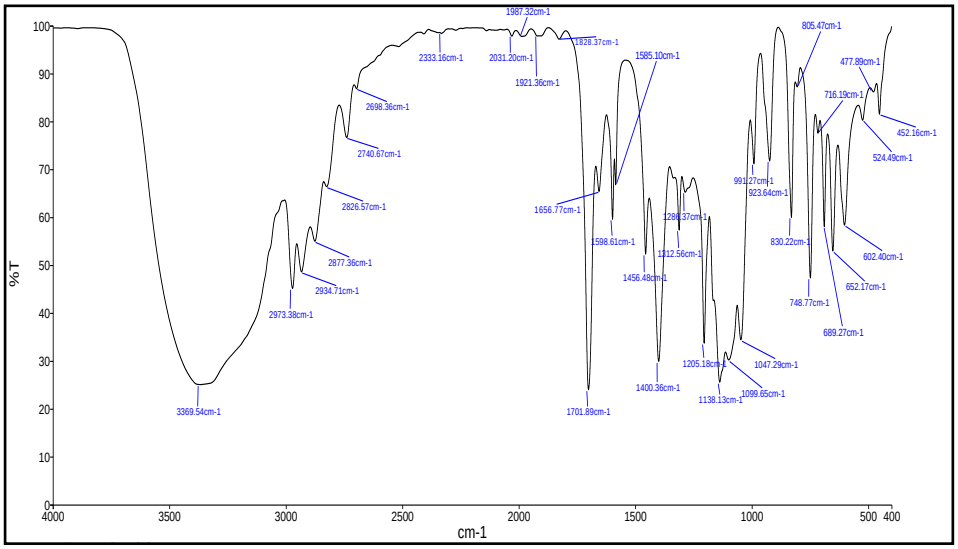

Fig. 5: FTIR – Spectra for Binary Liquid Mixtures of 1,2-Propanediol (1) + Benzaldehyde (2) at equimolar concentration.

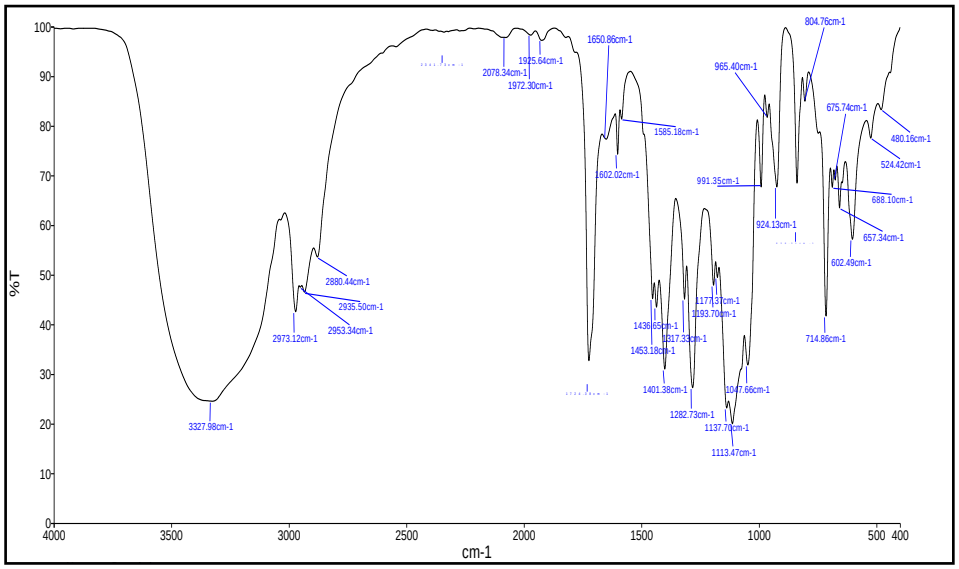

Fig. 6: FTIR – Spectra for Binary Liquid Mixtures of 1,2-Propanediol (1) + Methyl benzoate (2) at equimolar concentration

Conclusion

The densities and viscosities for binary liquid mixtures of 1,2-propanediol with cyclohexanone, benzaldehyde or methylbenzoate are determined experimentally, at 308.15 and 318.15 K over whole composition range. The value of V^E, $\Delta\eta$ and ΔG^{*E} are calculated from experimental results at both temperatures and fitted to Redlich-Kister type polynomial equation and corresponding standard deviation is calculated. From the observed negative values of V^E, $\Delta\eta$ and the positive values of ΔG^{*E} for the given analysed binary mixtures the following conclusions may be drawn:

1. The negative magnitude of V^E values suggest the formation of intermolecular hydrogen bonding and dipole-dipole interaction between the molecules.
2. The negative $\Delta\eta$ values that for 1,2-propanediol+cyclohexanone, + benzaldehyde show that the mixture is less viscous and positive $\Delta\eta$ values for 1,2-propanediol + methyl benzoate indicate that the mixture more viscous with reference to linear law.
3. ΔG^{*E} values reveal that there would be specific interaction between the component molecules.
4. The less positive values of ΔH indicate attractive interaction among the unlike molecules.
5. FT-IR spectra reveals the formation of intermolecular hydrogen bonding between unlike molecules.

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