Thermodynamical Study of Alcoholic Solutions of Poly (ethylene glycol) Diacrylate and Poly (ethylene glycol) Dimethacrylate

Maimoona Yasmin* and Manisha Gupta

Department of Physics, University of Lucknow, Lucknow, India- 226007
e-mail; myasmin908@gmail.com

Abstract

With the aim to study the behaviour of polymer solutions, density and ultrasonic velocity of binary mixtures of pentanol with polyethylene glycol diacrylate and polyethylene glycol dimethacrylate have been investigated at 293.15 K, 303.15 K and 313.15 K, under atmospheric pressure. Thermophysical parameters viz. intermolecular free length, internal pressure and pseudo-Grüneisen parameter have been calculated which infer about the interactions and structural changes on mixing pentanol with these polymers. Enthalpy, entropy and Gibbs free energy of activation for viscous flow at different concentrations of polymer solution have been reported. Excess molar volume, deviation in isentropic compressibility, deviation in ultrasonic velocity, excess acoustic impedance and excess molar enthalpy have been calculated and results have been correlated with Redlich-Kister polynomial equation. Density and ultrasonic velocity data have been fitted by third order polynomial equation.

Keywords: Poly (ethylene glycol) diacrylate; poly (ethylene glycol) dimethacrylate; density; ultrasonic velocity.

1. Introduction

Polyethylene glycol diacrylate (PEGDA) is a low volatility and medium viscosity clear liquid with good flexibility and elongation, good water dispersible property, low skin irritancy and good reactivity. It is used in flexible coatings, overprinting varnishes, offset inks and photopolymeric printing plates. PEGDA is soluble in water and is used as a functional co-monomer for flexible plastics and as a crosslinking agent between the molecular chains of polymers. PEGDA is able to effectively seal the vessel puncture sites and anastomotic junctions without acutely augmenting local vascular thrombogenicity (G.A. Dumanian et al.,1995).

Polyethylene (glycol) dimethacrylate (PEGDMA) is used in adhesives, coatings, sealants, photoresists, solder masks and photopolymers. It also contributes to flexibility.

1-Pentanol is a colorless liquid. To reduce the use of fossil fuels, research is underway to discover cost effective methods of utilizing fermentation to produce Bio-Pentanol. Pentanol can be used as a solvent for coating CDs and DVDs. Another use is a replacement for gasoline.

Such importance of these polymers and their solutions and its vast domain of industrial and biochemical applications have enforced us to study the means of predicting their properties. In the present work solutions of PEGDA and PEGDMA in pentanol have been studied. The aim of this work is to obtain information about the association among the components of mixtures under study, to investigate correlations among them and to provide qualitative interpretation in terms of molecular interactions. To our knowledge no density and velocity data have previously been reported for these mixtures.

Densities and ultrasonic velocities for the mixtures of pentanol + PEGDA and pentanol + PEGDMA have been reported at 293.15 K, 303.15 K and 313.15 K, under atmospheric pressure. Derived parameters such as intermolecular free length, internal pressure, pseudo-Grüneisen parameter, enthalpy, entropy and Gibbs free energy of activation for viscous flow at different concentrations of polymer solution have also been calculated using experimental data for both the systems. The intermolecular interactions present in the mixtures have been investigated through deviation in ultrasonic velocity, excess molar volume, deviation isentropic compressibility, excess molar enthalpy and excess acoustic impedance. The results have been fitted to Redlich-Kister polynomial equation. Density and ultrasonic velocity data have been fitted by third order polynomial equation. Similar studies have been done earlier by the workers and have been published in national and international journals(Yasmin and Gupta, 2011, M.Yasmin et al, 2011, S. Singh et. al. 2011, Gurung and Roy, 2006, Ciocirlan and Iuliana, 2009).

2. Experimental Procedures

2.1 Materials. The analytical grade chemicals PEGDA (Aldrich), PEGDMA (Aldrich) and pentanol (Sigma-Aldrich, ACS reagent, ≥99%) have been obtained from Sigma-Aldrich Chemicals Pvt. Ltd. The average molecular weight M_n of PEGDA 575 g.mol^{-1} and that for PEGDMA is 750 g.mol^{-1}. All chemicals were purified by standard procedure discussed by Perrin and Armarego (D.D. Perrin and W.L.F. Armarego, 1988). Solutions have been prepared by mass, using air tight bottles and have been measured on electronic balance OHAUS- AR 2104 (Ohaus Corp. Pine Brook, NJ, USA) with an accuracy of 1×10^{-4} g. The possible error in the estimation of mole fraction is less than ±0.0001.

2.2 Apparatus and procedures. Densities have been measured by a single capillary calibrated pycnometer, with a bulb capacity of 6.7 ml volume. The pycnometer stem contained graduation of 0.01ml. Pycnometer was immersed vertically in a double walled cylindrical water circulated glass jacket. The liquid rise in the capillary of pycnometer

was measured by travelling microscope (having a least count of 0.001 cm) for accuracy. The precision of the measured densities is of the order of $\pm 1 \times 10^{-4}$ g.cm^{-3}.

The interferometric technique has been used for the determination of ultrasonic velocity. The apparatus is a variable path fixed frequency (2 MHz) interferometer (Model F-81, Mittal Enterprises, New Delhi). It consists of a high frequency generator and a double walled measuring cell. A digital micrometer (with a least count of 0.001 mm) has been used to measure the distance between the reflector plate and the crystal within the cell. Once the wavelength is known, the ultrasonic velocity (u) in the liquid can be obtained using the following relation:

$$ultrasonic \ .velocity = frequency \times wavelength$$

The precision in the measurement of ultrasonic velocity is found to be 0.1 m.s^{-1}.

Circulating water bath with programmable temperature controller (TC-502, Brookfield Engineering Laboratories, Inc., USA), and variable pump speeds, has been used for water circulation around liquid cell of interferometer and water jacket of pycnometer. The programmable controllers incorporate an RS232 interface to provide remote data logging and control capability. The temperature controller covers the measurement range of temperature from -20°C to 200°C, with temperature stability of ± 0.01 $^{\circ}$C.

3. Results and Discussion

3.1 Experimental Results.
The experimentally measured values of density and ultrasonic velocity of pure liquids and their mixtures for the systems pentanol + PEGDA and pentanol + PEGDMA are reported in Table 1, as a function of concentration and temperature. In both the mixtures, both the density and ultrasonic velocity decrease non-linearly with increase in mole fraction of pentanol. Pentanol is highly self-associated through hydrogen bonds. Thus their structure and properties are determined mainly by quasi chemical bonds between the molecules, resulting in the formation of multimers of different size and structure. Mixing of polymer in pentanol enhances breaking of these self associated structures of pentanol and induces specific interaction between the components of the mixture.

Jacobson has shown that the intermolecular free length can be estimated from the experimental density and ultrasonic velocity data using the relation,

$$L_f = \frac{K}{u\rho^{1/2}} \tag{1}$$

where K is temperature dependent empirical constant, proposed by Jacobson.

The pseudo-Grüneisen parameter Γ, has been defined in terms of specific heat ratio as

$$\Gamma = \frac{\gamma - 1}{\alpha T} \tag{2}$$

where γ is specific heat ratio defined as

Table 1. Experimental values of densities ρ and ultrasonic velocities u for the systems pentanol + PEGDA and pentanol + PEGDMA at 293.15, 303.15 and 313.15 K with respect to the mole fraction x_1 of pentanol

x_1	T/K 293.15		T/K 303.15		T/K 313.15	
	ρ g.cm^{-3}	u m.s^{-1}	ρ g.cm^{-3}	u m.s^{-1}	ρ g.cm^{-3}	u m.s^{-1}
Pentanol + PEGDA						
0.0000	1.1206	1552.0	1.1133	1528.0	1.1018	1492.0
0.0993	1.1151	1544.0	1.1083	1520.0	1.0975	1484.0
0.2031	1.1070	1532.8	1.1006	1508.4	1.0899	1476.0
0.3389	1.0930	1518.3	1.0865	1496.0	1.0762	1464.0
0.4084	1.0840	1507.4	1.0774	1488.0	1.0671	1456.0
0.5025	1.0689	1482.3	1.0624	1469.4	1.0524	1440.0
0.5990	1.0490	1454.7	1.0427	1438.6	1.0329	1411.8
0.7018	1.0205	1410.6	1.0143	1396.9	1.0047	1370.3
0.7994	0.9818	1368.5	0.9757	1354.0	0.9670	1328.0
0.8981	0.9220	1332.4	0.9158	1308.4	0.9077	1275.2
1.0000	0.8147	1286.0	0.8078	1254.4	0.8007	1216.0
Pentanol + PEGDMA						
0.0000	1.1037	1548.0	1.0978	1516.0	1.0893	1488.0
0.1004	1.1010	1544.0	1.0956	1517.1	1.0880	1491.4
0.2050	1.0956	1533.4	1.0904	1505.4	1.0829	1480.8
0.3139	1.0881	1518.9	1.0832	1492.6	1.0756	1469.1
0.4000	1.0800	1507.2	1.0757	1479.3	1.0682	1455.8
0.5010	1.0678	1486.0	1.0638	1460.4	1.0566	1436.1
0.6002	1.0522	1460.0	1.0483	1435.6	1.0409	1408.0
0.6971	1.0300	1432.0	1.0261	1406.8	1.0188	1377.2
0.7990	0.9949	1393.9	0.9911	1374.6	0.9835	1344.0
0.9003	0.9351	1355.7	0.9303	1324.0	0.9226	1296.0
1.0000	0.8147	1286.0	0.8078	1254.4	0.8007	1216.0

$$\gamma = \frac{\beta_T}{\beta_S} \tag{3}$$

The relation utilized to estimate the internal pressure in pure liquids and liquid mixtures is

$$\pi_i = \frac{\alpha T}{k_T} \tag{4}$$

The parameters intermolecular free length (L_f), internal pressure (π_i) and pseudo-Grüneisen parameter (Γ) are temperature sensitive and provides significant information regarding intermolecular interaction between the component molecules in the mixtures. These parameters have been evaluated over the entire composition range for both the mixtures and have been represented in Figures 1 to 3.

The intermolecular free length (L_f), of the mixtures increases with increasing concentration of pentanol (figure 1). Breaking of self associated structures of pentanol occurs due to dissociation of hydrogen bonds in pentanol on mixing the components. The rate of increase of intermolecular free length also increases with increase concentration of pentanol. This may be due to the fact that pentanol is highly self associated by hydrogen bonding to the extent of polymerization. Hence the larger voids are formed by self-associated pentanol molecules than by PEGDA or PEGDMA molecules. PEGDMA molecules are larger than that of PEGDA hence intermolecular free length is larger in the system pentanol + PEGDMA than in pentanol + PEGDA. Rise in temperature makes the free length increase as expected due to thermal expansion of liquids.
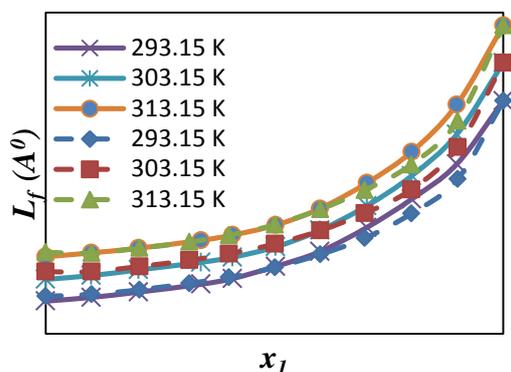
Figure 1. Intermolecular free length for the system pentanol + PEGDA (—) and pentanol + PEGDMA (---) at 293.15, 303.15 and 313.15 K with respect to the mole fraction of pentanol.
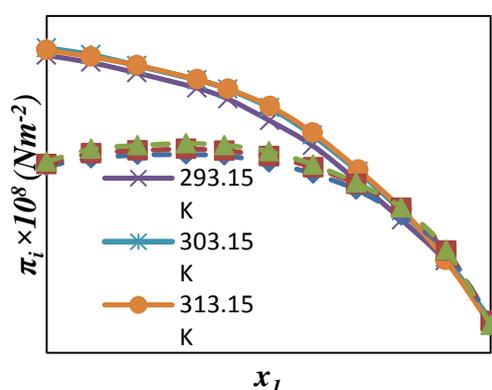
Figure 2. Internal pressure for the system pentanol + PEGDA (—) and pentanol + PEGDMA(---) at 293.15, 303.15 and 313.15 K with respect to the mole fraction of pentanol.
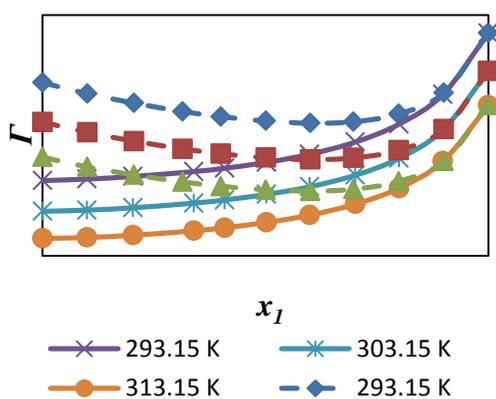
Figure 3. Pseudo-Grüneisen parameter for the system pentanol + PEGDA (—) and pentanol + PEGDMA (---) at 293.15, 303.15 and 313.15 K with respect to the mole fraction of pentanol.

The role of internal pressure (π_i) in solution thermodynamics was recognized many years ago by Hilderband following earlier work of Van Laar (J.M. Prausnitz, 1969). It has been found to be an important tool in the study of several chemical reactions and in the investigation of molecular interactions. The internal pressure of the mixture is found to vary non-linearly with

concentration of pentanol as listed in Figure 2. The internal pressure of the mixture decreases with increase in mole fraction of pentanol in the mixture. The internal pressure values increase slightly with rise in temperature as expected.

Pseudo-Grüneisen parameter (Γ) is one of the important parameter which is used to study internal structure, clustering phenomenon and thermodynamic properties of solid crystalline lattice. It is well established that liquids support a quasi-crystalline model for their structure, the lattice nature being increased at high pressure and low temperature hence the pseudo-Grüneisen parameter can also be used to study liquids. Figure 3 reveals that the pseudo-Grüneisen parameter of mixture decreases with increase in mole fraction of pentanol as well as with rise in temperature. The non-linear behaviour of this parameter suggests the presence of specific interaction in the mixtures. Similar variations in pseudo-Grüneisen parameter for the system THF + o-cresol have been also found (M. Yasmin et al., 2009).

The absolute rate theory based Eyring's kinematic viscosity model gives the relation

$$\eta V = N_A \, h \, exp \left(\frac{\Delta G^*}{RT} \right) \tag{5}$$

where η, V, N_A, h, R, T, ΔG^* are kinematic viscosity, molar volume, Avogadro's constant, Planck's constant, Universal gas constant, absolute temperature, and free energy of activation.

The entropy of viscous flow ΔS^*, enthalpy ΔH^* and Gibbs free energy of activation for viscous flow ΔG^* are related by the following equation

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{6}$$

The values of enthalpy, entropy and Gibbs free energy of activation for viscous flow at different concentrations of polymer solution have been given in Table 2.

Entropy of activation for viscous flow ΔS^* for both the systems is found to be negative. Enthalpy of activation of viscous flow ΔH^* on the other side is positive for all the three systems under study and values are about constant over the entire range of studied temperature for each concentration.

The values of ΔH^* are positive and of ΔS^* negative, indicating that the attainment of the transition state for viscous flow is accompanied by bond breaking. The entropy change of activation from the initial state to the transition at a given composition is significant during an activated viscous flow process; therefore this process is entropy-controlled for PEG solutions. It seems that for the viscous flow process, the structural factor dominates over the interactional one, as in the case of the mixing properties.

Gibbs free energy of activation for viscous flow ΔG^* increases with increase in temperature for the systems pentanol + PEGDMA and pentanol + PEGDA.

3.2 Excess parameters. The study on the possible change of thermodynamic properties of mixtures and their degree of deviation from ideality is an excellent qualitative and quantitative way to investigate about the molecular structure

Table 2. Calculated values of entropy of viscous flow, enthalpy and Gibbs free energy of activation for viscous flow at different concentrations of polymer solution for the systems pentanol + PEGDA and pentanol + PEGDMA at 293.15, 303.15 and 313.15 K.

x_1	ΔS^* kJmol^{-1}	ΔH^* kJmol^{-1}	ΔG^* kJmol^{-1} 293.15K	ΔG^* kJmol^{-1} 303.15K	ΔG^* kJmol^{-1} 313.15K
			pentanol+PEGDA		
0.0000	-33.73	34.866	44.798	45.071	45.453
0.0993	-39.47	32.644	44.268	44.561	45.040
0.2031	-40.31	31.800	43.664	43.982	44.451
0.3390	-43.24	30.040	42.762	43.119	43.608
0.4084	-42.97	29.596	42.229	42.591	43.075
0.5025	-40.53	29.554	41.464	41.815	42.266
0.5991	-46.30	26.878	40.493	40.885	41.403
0.7019	-47.06	25.438	39.270	39.656	40.204
0.7995	-52.97	22.313	37.884	38.332	38.928
0.8981	-52.70	20.551	36.008	36.504	37.064
1.0000	-50.04	19.152	33.842	34.357	34.820
			pentanol+PEGDMA		
0.0000	-43.32	33.327	46.065	46.388	46.930
0.1005	-46.69	31.881	45.602	45.978	46.535
0.2051	-50.72	30.158	45.076	45.459	46.085
0.3139	-50.81	29.476	44.426	44.804	45.436
0.4001	-49.60	29.240	43.823	44.208	44.810
0.5011	-49.23	25.833	43.015	43.407	43.984
0.6003	-51.51	27.157	42.003	42.395	43.013
0.6971	-53.57	25.056	40.837	41.170	41.900
0.7991	-53.77	23.364	39.242	39.502	40.295
0.9003	-53.97	21.164	37.027	37.427	38.113
1.0000	-50.04	19.152	33.842	34.357	34.820

and intermolecular forces in liquid mixtures. This has given impetus to the theoretical and experimental evaluation (S. Parveen et al., 2010) of the excess thermodynamic properties of liquid mixtures. Excess properties are sensitive towards external factors such as composition and temperature.

The excess parameters have been evaluated using following relations,

Deviation in ultrasonic velocity,

$$\Delta u = u - (x_1 u_1 + x_2 u_2) \tag{7}$$

Excess molar volume,

$$V^E = \left(\frac{x_1 m_1 + x_2 m_2}{\rho} \right) - \left(\frac{x_1 m_1}{\rho_1} + \frac{x_2 m_2}{\rho_2} \right) \tag{8}$$

Excess acoustic impedance,

$$Z^E = (\rho\, u\,) - (x_1 \rho_1 u_1 + x_2 \rho_2 u_2) \tag{9}$$

Excess isentropic compressibility,

$$\Delta k_s = \frac{1}{u^2 \rho} - \left(\frac{x_1}{u_1^2 \rho_1} + \frac{x_2}{u_2^2 \rho_2} \right) \tag{10}$$

Excess molar enthalpy,

$$H_m^E = x_1 \pi_{i1} V_1 + x_2 \pi_{i2} V_2 - \pi_i V \tag{11}$$

Excess molar volume, deviation in isentropic compressibility, deviation in ultrasonic velocity, excess acoustic impedance and excess molar enthalpy for the binary mixtures under study have been reported in Figures 4-8.
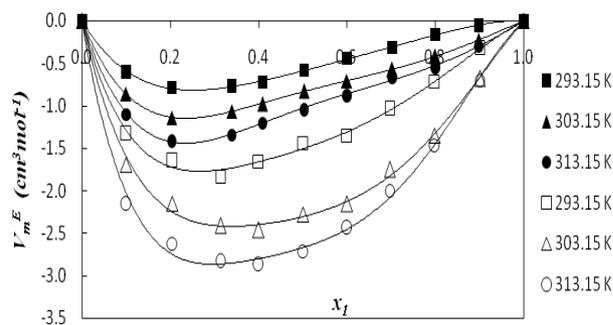
Figure 4. Excess molar volume for the system (■, ▲, ●) pentanol + PEGDA and (□, Δ, O) pentanol + PEGDMA at 293.15, 303.15 and 313.15 K with respect to the mole fraction of pentanol.

The excess molar volume V^E (Figure 4) for the systems pentanol+ PEGDA and pentanol+ PEGDMA are negative over entire composition range at all three temperatures. The large negative values arise due to increased interactions between PEGDMA or PEGDA and solvent or a very large difference in the molar volumes of the components. Treszczanowicz et al (A.J. Treszczanowicz et al., 1981) suggested that V^E is the result of contributions from several opposing effects, namely, physical, chemical, and structural. Physical contributions, which are non specific interactions between the real species present in the mixture, contribute a positive term to V^E. The chemical or specific intermolecular interactions result in a volume decrease. This effect contributes negative values to V^E. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes in the free volume. In other words, structural contributions arising from the geometrical fitting (interstitial accommodation) of one component into other due to the differences in the free volumes and molar volumes between components lead to negative contribution to V^E. The actual value of V^E would depend on the relative strengths of these effects. The experimental values of V^E suggest that interstitial accommodation is leading to the negative values while increase in negative values with temperature suggest that structural effect is more prominent than chemical effect in these solutions because of the large difference in molar volumes between components. The larger difference in molar volume of components in the system pentanol+ PEGDMA than that in the system pentanol + PEGDA (108.18, 513.09 and 679.48 cm^{3}mol^{-1} for pentanol, PEGDA and PEGDMA respectively at 293.15 K) results in larger excess molar volumes. Earlier workers have also concluded the above result for polymer solutions (M.T. Zafarani-Moattar and N. Tohidifar, 2008). The increase in negative values of V^E with temperature reflects that thermal energy enhances the strength of interaction.

Deviations in isentropic compressibility Δk_s, Figure 5, is to be negative over whole composition range. Thus it can be concluded that mixing of pentanol with PEGDA and

PEGDMA respectively results in enhanced rigidity. In liquid phase a molecule of pentanol is able to build up at most two hydrogen bonds with its next neighbours to form open cyclic polymeric chains of various lengths. Mixing of polymers causes more compact structure due to interstitial accommodation of component molecules. Fort and Moore (R.J. Fort and W.R. Moore 1955). has shown earlier that liquids of different molecular size usually mix with decrease in volume resulting in negative Δk_s values. Similar results have been found by Singh *et al* (K. P. Singh et al., 2009) for the binary mixtures of 2-butoxyethanol with PEG 200 and PEG 400.
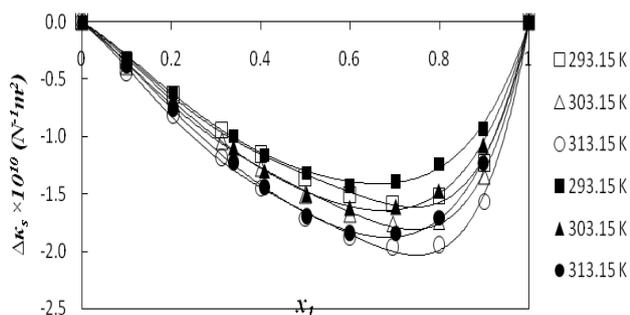
Figure 5. Deviation in isentropic compressibility for the system (■,▲,●) pentanol + PEGDA and (□ , Δ, O) pentanol + PEGDMA at 293.15, 303.15 and 313.15 K with respect to the mole fraction of pentanol.
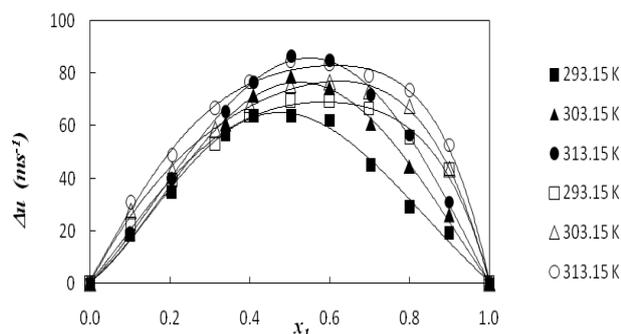
Figure 6. Deviation in ultrasonic velocity for the system (■,▲,●) pentanol + PEGDA and (□ , Δ, O) pentanol + PEGDMA at 293.15, 303.15 and 313.15 K with respect to the mole fraction of pentanol.

Due to intermolecular interactions structure of the molecule is changed, which affect the compressibility and thus a change in ultrasonic velocity. The ultrasonic velocity in a mixture is mainly influenced by the free length between the surfaces of the molecules of the mixture. The inverse dependence of intermolecular free length and ultrasonic velocity has been evolved from the model of sound propagation proposed by Eyring and Kincaid (J.F. Kincaid and H. Eyring, 1937). As shown in Figure 6, deviation in ultrasonic velocity Δu is positive for the mixtures. Our results for intermolecular free length and deviation in ultrasonic velocity support this theory. This kind of variations suggests that significant interactions are operative in these mixtures as also studied by Ali and Tariq (A. Ali and M. Tariq, 2006) for the system benzyl alcohol with benzene. The increase in Δu with temperature suggests that thermal energy enhances the strength of interaction.
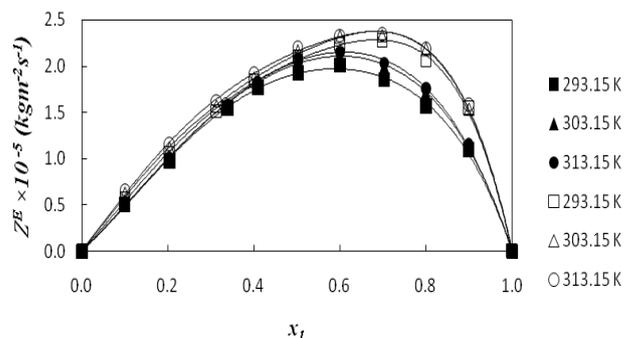
Figure 7. Excess acoustic impedance for the system (■,▲,●) pentanol + PEGDA and (□ , Δ, O) pentanol + PEGDMA at 293.15, 303.15 and 313.15 K with respect to the mole fraction of pentanol.
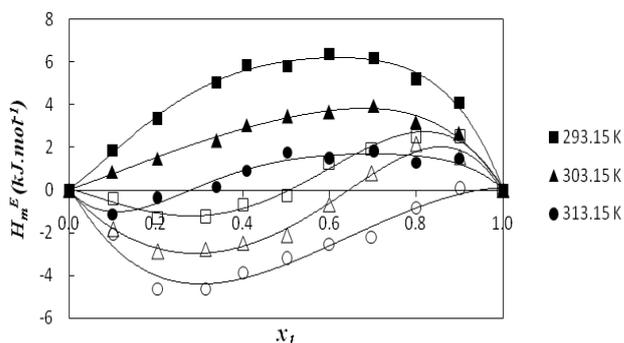
Figure 8. Excess molar enthalpy for the system (■,▲,●) pentanol + PEGDA and (□, Δ, O) pentanol + PEGDMA at 293.15, 303.15 and 313.15 K with respect to the mole fraction of pentanol.

Specific acoustic impedance is a quantity, which depends on the molecular packing of the systems. It can be seen from Figure 7 that the values of excess acoustic impedance Z^E are positive for both the mixtures which indicate the presence of specific intermolecular interaction through hydrogen bonding between the unlike species. The effect of temperature on Z^E is not very prominent in all the mixtures. The values are more positive for the system pentanol+ PEGDMA as compared to pentanol+ PEGDA suggesting the interaction to be stronger in solution of PEGDMA than in that of PEGDA.

The excess molar enthalpy H_m^E curve (Figure 8) has been found to be *S*- shaped for pentanol+ PEGDMA mixture and positive for pentanol+ PEGDA mixture. The values of H_m^E for pentanol + PEGDMA are negative in polymer rich region and turn to be small positive in pentanol rich region. The negative values of H_m^E in the case of pentanol + PEGDMA mixture indicate the presence of strong intermolecular interaction between unlike molecules. However, positive values of H_m^E suggest that the effect of rupture of hydrogen bonded chain of pentanol dominates over the specific interactions between pentanol and PEGDMA molecules. This may also be due to greater steric hindrance caused by methyl groups attached in the PEGDMA molecules. The negative values of H_m^E decreases as temperature increases in the case of pentanol + PEGDMA mixture. However, positive H_m^E values in the case of pentanol+ PEGDA mixture decreases as temperature increases which suggests decrease in self association of the pure component and increase in strength

of interaction with temperature. Increase in temperature will cause rupture of more and more H-bonded self association in pentanol molecules and also hetero association between unlike molecules. This reduces the positive deviation with increase in temperature.

The observed variation in these thermodynamic parameters in the present investigation may be result of contribution from several effects such as:
1. The breakdown of self associated structures of pentanol.
2. The specific interactions in the systems pentanol+ PEGDMA and pentanol+ PEGDA
3. Structural contribution arising from the geometrical fitting of molecules of one component into the voids forms by the molecules of other.

3.3 Redlich-Kister polynomial equation.
The composition dependences of the excess properties are correlated by the Redlich-Kister polynomial equation (O. Redlich and A.T. Kister, 1984)

$$Y^E = x_1(1 - x_1)\sum_{i=1}^{5} a_i(2x_1 - 1)^{i-1} \tag{12}$$

The values of the coefficient a_i were calculated by method of least squares along with the standard deviation $\sigma(Y^E)$. The coefficient a_i is adjustable parameters for a better fit of the excess functions.

The standard deviation values were obtained from relation

$$\sigma(Y^E) = \left[\frac{\sum_{i=1}^{n}\left(Y_{expt}^E - Y_{cal}^E\right)^2}{n - p}\right]^{1/2} \tag{13}$$

where n is the no. of experimental points, p is the no. of parameters, Y_{expt} and Y_{cal} are the experimental and calculated parameters respectively. The values of co-efficient a_i evaluated using the method of least squares for the mixtures are given in Table 3 along with the standard deviations $\sigma(Y^E)$.

3.4 Data Correlation.
The density and ultrasonic velocity data are fitted by the following relations

$$\rho/g.cm^3 = ax_1^3 + bx_1^2 + cx_1 + d \tag{14}$$

$$u/ms^{-1} = a'x_1^3 + b'x_1^2 + c'x_1 + d' \tag{15}$$

where ρ and u are the density and ultrasonic velocity of the solution at the measured temperature, a, b, c and d are the coefficients of the polynomial in gcm^{-3} a', b', c' and d' are the coefficients of the polynomial in ms^{-1} and x_1 is the mole fraction of the polymer in the solution.

Values of the coefficients are obtained by regression. The coefficients in the equation 14 and 15 along with the percentage average absolute deviations (%AAD) calculated using equation 16 are given in Tables 4 and 5.

Table 3. Coefficients of the Redlich-Kister equation for excess parameters and their standard deviation for the system pentanol + PEGDA and pentanol + PEGDMA

Parameters	T/ K	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^E)$
			pentanol+PEGDA				
$V_m^E \times 10^{-6}/$ (m^3.mol^{-1})	293.15	-2.3419	-2.3676	-1.1799	-2.3029	-1.2443	0.0097
	303.15	-4.1909	-7.5774	-8.9660	5.2195	10.1736	0.3269
	313.15	-4.0957	-3.5170	-6.7300	-3.2042	1.7138	0.0323
$\Delta k_s \times 10^{-10}/$(N^{-1}m^2)	293.15	-5.1555	2.0441	-0.2689	3.4236	-3.7952	0.0089
	303.15	-6.0359	3.5958	0.2715	2.2501	-4.7917	0.0050
	313.15	-6.7231	4.3271	-1.2736	2.3478	-3.0795	0.0106
$\Delta u/$ (m.s^{-1})	293.15	265.9901	69.8559	-335.9051	-115.4274	388.6938	1.5115
	303.15	316.4021	-62.9194	-293.2690	27.2195	292.8781	0.5887
	313.15	339.2848	-104.3641	-100.7280	40.1547	0.9336	1.2774
Z$^E \times 10^{-3}/$(kg.m^{-2}.s^{-1})	293.15	7.7240	-1.9118	-1.1733	-3.3757	4.6233	0.0157
	303.15	8.2235	-3.3410	-1.3311	-1.4415	4.4314	0.0073
	313.15	8.2923	-3.3860	0.6839	-1.5270	1.0790	0.0154
$H_m^E/$ (kJ.mol^{-1})	293.15	23.4799	-4.0431	-4.2105	-17.0379	30.7781	0.2177
	303.15	13.3327	-32.4870	-50.3619	31.7156	94.0715	0.1611
	313.15	10.2706	-49.2561	59.4002	49.6605	-114.5839	0.2777
			pentanol+PEGDMA				
$V_m^E \times 10^{-6}/$ (m^3.mol^{-1})	293.15	-5.8832	-3.9235	-5.7787	-4.5277	1.2148	0.0696
	303.15	-10.6823	-0.7168	3.7517	-9.7382	-11.8859	0.0444
	313.15	-10.8614	-3.7187	-6.1229	-9.9667	-2.7296	0.0182
$\Delta k_s \times 10^{-10}/$(N^{-1}.m^2)	293.15	-5.4554	2.4907	-1.3545	5.9445	-5.9520	0.0053
	303.15	-6.0177	3.7438	-2.8602	4.5498	-4.4420	0.0087
	313.15	-6.9236	3.8599	-1.5874	6.1359	-7.9408	0.0103
$\Delta u/$ (m.s^{-1})	293.15	277.7313	-16.9259	-76.5531	-205.5004	334.1284	0.9966
	303.15	324.4851	-420.2246	314.2025	940.9104	-975.4218	11.6873
	313.15	373.3022	228.0240	401.0586	-601.4012	-407.0663	0.3807
Z$^E \times 10^{-3}/$(kg.m^{-2}.s^{-1})	293.15	8.3777	-3.4936	1.6726	-5.0429	5.6705	0.0087
	303.15	8.5904	-4.5825	3.5882	-2.2668	2.8949	0.0099
	313.15	8.7533	-3.9797	2.9046	-3.6790	4.5697	0.0121
$H_m^E/$ (kJ.mol^{-1})	293.15	1.3471	-19.8274	-5.1583	-0.5210	32.8853	0.2234
	303.15	-0.3106	37.7858	106.7547	-96.5269	-171.4546	0.2367
	313.15	-6.8308	-25.2372	-54.6883	16.6202	75.1354	0.0954

Table 4. Coefficients of polynomial equation (14) for the systems pentanol + PEGDA and pentanol + PEGDMA at 293.15, 303.15 and 313.15 K.

T/K	a	b	c	d	%AAD	Max%D
			Pentanol + PEGDA			
293.15	-0.588	0.481	-0.196	1.125	-0.0811	0.8854
303.15	-0.591	0.483	-0.194	1.118	-0.0375	1.0136
313.15	-0.582	0.472	-0.188	1.107	-0.0049	1.0353
			Pentanol + PEGDMA			
293.15	-0.716	0.646	-0.214	1.110	-0.0678	1.3763
303.15	-0.734	0.664	-0.215	1.105	-0.0004	1.5087
313.15	-0.727	0.652	-0.208	1.096	-0.0195	1.5349

Table 5. Coefficients of polynomial equation (15) for the systems pentanol + PEGDA and pentanol + PEGDMA at 293.15, 303.15 and 313.15 K

T/K	a'	b'	c'	d'	%AAD	Max %D
			Pentanol + PEGDA			
293.15	59.42	-345.80	21.88	1548	-0.0096	0.4600
303.15	-78.88	-185.70	-8.64	1524	-0.0423	0.4528
313.15	-165.90	-89.02	-21.26	1489	-0.0137	0.3624
			Pentanol + PEGDMA			
293.15	-178.60	0.35	-80.95	1550	-0.0038	0.6386
303.15	-222.90	40.95	-79.04	1519	-0.0609	0.0458
313.15	-216.70	3.46	-56.01	1492	-0.0095	0.7545

$$\% AAD = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{A_{cal} - A_{exp}}{A_{exp}} \right| \tag{16}$$

where A_{cal} and A_{exp} is calculated and experimental density and velocity respectively.

4. Conclusions

It can be concluded from the above results that there is a presence of specific intermolecular interaction in both the systems. The interaction is found to be stronger in the system pentanol + PEGDMA than in pentanol + PEGDA. The difference in molar volumes of the components is much large hence the structural effect is most prominent in these mixture properties.

The correlation data reported in the paper can be used further in industry or research for theoretical modeling and for studying the mixture further at concentrations other than those reported.

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