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Interaction study of 1-hexanol + cyclohexane + n-heptane ternary system at 298.15 K from excess volume and sound velocity data

Sonu Dwivedi**Abstract**

Densities and speed of sound were measured for the ternary liquid mixtures formed by 1-Hexanol, Cyclohexane and n-Heptane at 298.15K and atmospheric pressure over the whole concentration range. Flory model was applied to study the mixing properties and interactions in these liquids. Deviations in the speed of sound and excess molar volume were evaluated and fitted to the Redlich-Kister polynomial equation to derive the binary coefficients and standard errors. An attempt has also been made to study the molecular interactions involved in the liquid mixture from the observed data. Furthermore, excess molar volume and isentropic compressibility for these ternary mixture were computed and correlated with the observed data. Conclusively, it was found that Flory model (non-associated) provides good result when compared with the observed properties.

Keywords: Densities, excess molar volume, isentropic compressibility, liquid mixture

1. Introduction

The Knowledge of structure and molecular interaction of liquid mixtures has been very important from the fundamental and engineering points of view. Liquid mixtures rather than pure liquids find practical application in many industries because mixing gives flexibility to alter the properties (with in a reason able range) by varying the composition and concentration. Mixing of liquids introduces some extra degree of freedom and result in new phenomena which are not present in pure liquids such as complex formation, association, dissociation etc. This difference between actual properties and properties if system behaves ideally is known as excess properties ^[1]. It indicates that the molecules of solute and solvent interact when mixed with each other and exhibit the non-ideal behavior. Thus, the mixing process considerably affects the molecular interaction between component molecules ^[2-3]. Many researchers pointed out the importance of examination of consequences of mixing process ^[4-5]. Thermo-actual properties and sub-atomic associations of fluids and fluid blends can be considered by sound velocity ^[6-8, 10-13]. Broad work has been completed by numerous workers ^[9-12] to concentrate on the cooperation's and sub-atomic way of behaving through sound speed information and to relate with other physical and thermodynamic boundaries. These information were examined as far as Flory model ^[13]. For this reason, I chose the non-electrolite fluids of ternary blends containing alkanol – cycloalkane -alkane containing long carbon chain (non-polar) and alkanol isomer (polar) particles and cyclic alkane. From these results, deviations in ultrasonic speed not entirely settled and fitted to the Redlich-Kister polynomial condition ^[14] to induce the coefficients and the standard mistakes.

The current work meant to study the acoustical and volume properties of non-electrolyte ternary combination containing alkanol-cycloalkane-alkane and their sub-atomic collaborations with the assistance of Flory model. Here, I present the test and hypothetical consequences of speed of sound, isentropic compressibility and abundance molar volume for ternary fluid combinations; in particular; 1-Hexanol, Cyclo-hexane and n- Heptane at 298.15K and atmospheric pressure over the whole piece. 1-Hexanol is produced industrially by the oligomerization of ethylene using triethylaluminium followed by oxidation of the alkylaluminium products. It also is partly responsible for the fragrance of strawberries ^[15]. It is additionally used to assess the lipophilicity of drug products ^[16]. Cyclohexane is utilized as a non-polar dissolvable in the synthetic industry ^[17-28] and furthermore as an unrefined substance for the modern creation of adipic corrosive and caprolactam, the two of which are intermediates utilized in the development of nylon.

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As well as being utilized as fuel. Heptane has various modern purposes. n-Heptane (and its many isomers) is widely used in laboratories as a non-polar solvent. As a liquid, it is ideal for transport and storage. In the grease spot test. n-Heptane is used to dissolve an oil spot to show the previous presence of organic compounds on a stained paper. This is done by shaking the stained paper in a heptane solution for about half a minute. n-Heptane is commercially available as mixed isomers for use in paints and coatings, as the rubber cement solvent "Bestine", the outdoor stove fuel "Powerfuel" by Primus, as pure n-heptane for research and development and pharmaceutical manufacturing and as a minor component of gasoline (petrol) [19].

2. Experimental section

2.1 Materials

High virtue and AR grade tests of 1-Hexanol, Cyclo-hexane and n-Heptane utilized in this test were acquired from Merck Co. Inc., Germany and decontaminated by refining in which the middle fraction was gathered. The solvents were taken care of in faint containers over 0.4nm atomic strainers to limit water content and were most of the way degassed with a vacuum siphon. The immaculateness of each compound was checked by gas chromatography and the outcomes demonstrated that the mole division virtue was higher than 0.99. The immaculateness of synthetic substances utilized was affirmed by contrasting the densities and ultrasonic paces and those revealed in the writing as displayed in Table 1.

2.2 Apparatus and procedure

Before every series of examinations, I aligned the instrument at barometrical strain with doubly refined water. The vulnerability in the density estimation was inside $\pm 6.10^{-4} \text{ g.cm}^{-3}$. The densities of the unadulterated parts and their combinations were estimated with the bi-narrow pyknometer. The fluid blends were ready by mass in an impenetrable halted bottle utilizing an electronic equilibrium model Shimadzuax-200 exact to inside $\pm 0.1 \text{ mg}$. The normal vulnerability in the piece of the combinations was assessed to be under ± 0.0001 . All molar amounts depended on the overall nuclear mass table. Gem controlled variable way ultrasonic interferometer provided by M/s Mittal ventures (model-05F), New Delhi (India), working at a recurrence of 2 MHz was utilized in the ultrasonic estimations and the vulnerability was inside $\pm 3 \text{ m.s}^{-1}$ which are reproducible. Isentropic compressibility, β_s , were determined from the Laplace equation as;

$$\beta_s = u^{-2} \rho^{-1} \quad (1)$$

Where

ρ is the thickness and u is the ultrasonic speed. The assessed blunder in the estimation of isentropic compressibility was viewed as $\pm 2.5 \text{ T Pa}^{-1}$. The results are recorded in Table 1 along with writing values [20] for examination.

3. Theoretical

Flory and co-worker utilized the cell segment work and a straightforward van der Waals energy-volume connection by putting $m = 3$, $n = \infty$ in the cell model of Prigogine [21] and acquired the conditions for the blending capacities by

settling on this specific decision of m , n potential. Patterson *et al.* [22] have laid out a nearby connection between the Flory hypothesis and relating state hypothesis of Prigogine [23] utilizing a straightforward cell model for the round chain atoms of fluid state in a type of decrease boundaries. With the specific $(3, \infty)$ decision of m , n potential, eq. accepts the structure as;

$$\sigma v = \left[M v^{\sim -5/3} - \left(\frac{\tilde{v}^{1/3} - 1.0}{v^2} \right) \ln \left(\frac{\tilde{v}^{1/3} - 0.5}{\tilde{v}^{1/3} - 1.0} \right) \right] \quad (2)$$

Hence the Surface strain of fluid blend is given by the articulation as;

$$\sigma = \sigma^* \tilde{\sigma}(\tilde{v}) \quad (3)$$

and surface tension is related to the acoustic velocity by the empirical relation of Auerbach [24] as;

$$u_{\text{Flory}} = \left(\frac{\sigma}{6.3 \times 10^{-4} \rho} \right)^{2/3} \quad (4)$$

In order to extend the corresponding state theory to deal with the surface tension, Patterson and Rastogi [22] used the reduction parameters as,

$$\sigma^* = k^{1/3} P^{*2/3} T^{*1/3} \quad (5)$$

called the trademark surface pressure of the fluid. Here k is the Boltzmann steady. A portion an expansion in the configurational energy equivalent to $-M U(v)$ ~because of mass stage to the surface stage. It's most reasonable worth reaches from 0.25 to 0.29. Flory inferred the diminished condition of state from the subsequent parcel work as,

$$\frac{\tilde{P} \tilde{v}}{T} = \frac{\tilde{v}^{\sim 1/3}}{v - 1} - \frac{1}{v \tilde{T}} \quad (6)$$

The reduced quantities v , P and T are given by,

$$\tilde{P} = \frac{P}{P^*} = \frac{2PV^*}{S\eta}, \quad \tilde{T} = \frac{T}{T^*} = \frac{2V^* cKT}{S\eta} \quad \text{and} \quad \tilde{v} = \frac{V}{V^*} = \frac{v}{v^*} \quad (7)$$

From eq. (7), the reduced molar volume and characteristic pressure are given as;

$$\tilde{v} = \left[\frac{\alpha T}{(3 + 3\alpha T)} + 1 \right]^3, \quad P^* = \frac{\alpha}{\beta_T} T \tilde{v}^2 = y T \tilde{v}^2 \quad (8)$$

Where

α , β_T and y are thermal expansion coefficient, isothermal compressibility and the thermal pressure coefficient respectively. The quantities T^* , P^* , and V^* can be computed from α , β_T and V as prescribed by eqs. (7) and (8). Pandey *et*

al. [25] have formulated the equations for characteristic pressure and reduced temperature of mixture as;

$$\tilde{T} = T / T^* = \frac{T}{P^* / \left(\frac{\psi_1 P^*}{T_1^*} + \frac{\psi_2 P^*}{T_2^*} + \frac{\psi_3 P^*}{T_3^*} \right)} \quad (9)$$

Where

P^* is the characteristic pressure of binary system and can be expressed as

$$P^* = [\psi_1 P^* + \psi_2 P^* + \psi_3 P^* - (\psi_{12} \theta_{12} X_{12} + \psi_{23} \theta_{23} X_{23} + \psi_{31} \theta_{31} X_{31})] \quad (10)$$

Here x_{12} , x_{21} are the association boundaries which have been figured on utilizing the accompanying conditions by embracing natural Berthelot relationship for example $\eta_{ij} = (\eta_{ii} \eta_{jj})^{1/2}$. All the documentations utilized in the above conditions have their standard importance as itemized out by Flory. The abundance volume of paired fluid blend can be gotten by the situation as;

$$\tilde{v} - \tilde{v}_0 = \frac{v^E}{x_1 v_1^* + x_2 v_2^* + x_3 v_3^*} \quad (11)$$

Where

v_0 is the ideal reduce volume and it is given as;

$$\tilde{v}_0 = \psi_1 \tilde{v}_1 + \psi_2 \tilde{v}_2 + \psi_3 \tilde{v}_3 \quad (12)$$

replacement of eq.(11) in eq.(12) straightforwardly gives the abundance volume of double framework with slight reworking which can be addressed as

$$v^E = [(x_1 v_1^* + x_2 v_2^* + x_3 v_3^*) \tilde{v} - (\psi_1 \tilde{v}_1 + \psi_2 \tilde{v}_2 + \psi_3 \tilde{v}_3)] \quad (13)$$

Where

v^E is the overabundance molar volume and is the decreased molar volume of the parallel fluid combinations, expecting that the volume decrease boundaries of the double blends to be direct in mole division as;

$$\tilde{v} = \frac{v}{x_1 v_1^* + x_2 v_2^* + x_3 v_3^*}, \quad \rho = \frac{M_1 x_1 + M_2 x_2 + M_3 x_3}{\rho} \quad (14)$$

Table 3: Trial densities, ρ_{exp} estimated and hypothetical speed of sound, u_{exp} , u_{Theo} their percent deviation, % Δu , isentropic compressibilities, β_s , overabundance isentropic compressibilities β_s^E , noticed abundance molar volume, V^E and hypothetical overabundance molar volume, V^E for 1-Hexanol+Cyclohexane+n-Heptane ternary framework at 298.15K

x1	x2	$\rho_{exp} / \text{g.cm}^{-3}$	$u_{exp} / \text{m.s}^{-1}$	$u_{Theo} / \text{m.s}^{-1}$	% Δu	$\beta_s / \text{TPa}^{-1}$	$\beta_s^E / \text{TPa}^{-1}$	$V^E / \text{cm}^3 \text{.mol}^{-1}$	$V^E \text{ Theo} / \text{cm}^3 \text{.mol}^{-1}$
0.9123	0.0552	0.8156	1279.4	1238.2	3.22	574	-14	-0.028	-0.039
0.8012	0.0834	0.8104	1248.6	1205.8	3.43	598	-21	0.048	0.061
0.7178	0.1828	0.8040	1235.2	1188.6	3.77	625	-20	0.069	0.067
0.6087	0.2721	0.8006	1207.4	1158.3	4.06	654	-17	0.175	0.185
0.5128	0.3956	0.7958	1177.9	1134.7	3.67	677	-16	0.256	0.267
0.4149	0.4576	0.7905	1151.8	1103.9	4.15	697	-14	0.338	0.346
0.2773	0.6058	0.7854	1138.9	1091.5	4.16	718	-09	0.365	0.404
0.1248	0.7024	0.7801	1099.4	1055.9	3.95	736	-07	0.345	0.392
0.0914	0.8248	0.7785	1056.8	1017.1	3.75	757	-06	0.257	0.293

Where

V , ρ , M are the molar volume, thickness and molar mass of the fluid combination individually. The previously mentioned condition has been used for the calculation of abundance volume of double fluid blends. Every one of the documentations utilized in the above conditions have their standard importance as detailed out by Flory.

4. Results and Discussion

Test upsides of thickness and speed of sound, for the unadulterated fluids at various temperatures are recorded in Table 1 for correlation with writing values [20]. Isentropic compressibility's, β_s (determined through the Laplace condition) and abundance isentropic compressibility's, β^E for ternary fluid combination were assessed and recorded in Table 3. Values of thermal expansion coefficient (α) and isothermal compressibility (β_T) were gotten by and tested [26] condition. Abundance extents, either overabundance molar volumes, V^E , or abundance isentropic compressibility's, β_s^E , were determined utilizing the accompanying condition.

$$Q^E = Q - Q_{id} \quad (15)$$

Table 1: Warm development coefficient, α , isothermal compressibility, β_T , molar volume V_m , densities, ρ and rates of sound, u of unadulterated parts for examinations at 298.15K

Components	$\alpha \cdot 10^{-3} / \text{K}^{-1}$	$\beta_T / \text{TPa}^{-1}$	$V_m / \text{cm}^3 \text{.mol}^{-1}$	$\rho / \text{g.c}^{-3} \text{m}$		$u / \text{m.s}^{-1}$	
				Exp	Lit	Exp	Lit
1-Hexanol	1.1876	81.24	128.04	0.8151	0.8149	1303.7	1303.0
Cyclohexane	1.2150	114.0	108.76	0.7732	0.7738	1251.1	1254
n-Heptane	1.3572	178.3	147.47	0.6796	0.6795	1131.0	1131.5

Table 1 should be placed under the sub heading Materials

Table 2: Coefficient of Redlich-Kister (a , b , c) and standard deviation, δ , for ternary fluid combinations (1-Hexanol + Cyclohexane + n-Heptane) at 298.15K

	A	B	C	Δ
$V^E (\text{cm}^3 \text{mol}^{-1})$	-0.857	2.465	2.245	0.003
$\beta_s / \text{TPa}^{-1}$	-186	401	403	0.875

Table 2 should be placed just after Eq.17 under heading Results and Discussion

0.7878	0.0934	0.7714	1261.2	1206.0	4.37	778	-41	-0.179	-0.192
0.6021	0.1787	0.7687	1248.4	1198.2	3.31	792	-38	-0.028	-0.058
0.4758	0.3214	0.7634	1231.5	1172.4	4.02	811	-30	0.104	0.114
0.4187	0.4286	0.7604	1169.8	1128.6	3.52	825	-26	0.168	0.231
0.3688	0.4985	0.7574	1110.3	1066.7	3.92	854	-22	0.265	0.283
0.1836	0.6245	0.7534	1084.8	1039.6	4.17	877	-20	0.248	0.302
0.0820	0.7644	0.7487	1067.4	1024.1	4.05	898	-19	0.235	0.258
0.5642	0.0785	0.7754	1106.8	1065.4	3.74	912	-48	-0.244	-0.247
0.4548	0.1826	0.7636	1142.7	1098.2	3.89	887	-50	-0.087	-0.104
0.3754	0.2867	0.7618	1151.6	1108.1	3.78	899	-42	0.032	0.066
0.2687	0.4113	0.7524	1124.9	1086.8	3.38	906	-37	0.175	0.177
0.1842	0.5145	0.7465	1113.8	1075.3	3.45	928	-30	0.244	0.225
0.0835	0.6254	0.7358	1109.4	1062.8	4.20	967	-25	0.234	0.247
0.4658	0.0824	0.7564	1088.1	1047.6	3.72	880	-67	-0.268	-0.294
0.3102	0.1854	0.7538	1071.6	1036.2	3.30	905	-54	-0.114	-0.116
0.2546	0.3247	0.7488	1051.5	1015.8	3.39	936	-49	0.034	0.039
0.1836	0.4321	0.7395	1043.5	1004.3	3.75	958	-41	0.134	0.136
0.0980	0.5047	0.7329	1086.4	1045.3	3.78	979	-34	0.148	0.198
0.3654	0.0795	0.7278	1128.9	1088.8	3.56	1002	-62	-0.247	-0.234
0.2547	0.1785	0.7021	1112.6	1077.4	3.16	1024	-54	-0.102	-0.108
0.1598	0.2754	0.6987	1086.4	1051.4	3.22	1039	-39	0.056	0.039
0.0869	0.4345	0.6920	1071.8	1034.6	3.47	1057	-30	0.145	0.137
0.2954	0.1312	0.6875	1052.8	1016.3	3.46	1068	-58	-0.234	-0.218
0.1387	0.1878	0.6812	1121.5	1085.3	3.22	1086	-46	-0.073	-0.084
0.0866	0.2987	0.6757	1101.9	1062.2	3.50	1097	-32	0.084	0.082
0.1820	0.1354	0.6710	1086.7	1037.8	3.60	1124	-43	-0.156	-0.152
0.0734	0.2254	0.6675	1068.9	1029.4	3.69	1148	-31	0.005	0.013
0.0885	0.1287	0.6613	1046.8	1011.2	3.59	1176	-27	-0.045	-0.081
0.0698	0.0897	0.6524	1039.8	1004.8	3.36	1208	-10	-0.036	-0.042

$$V^{E I} = \sum_{i=1}^n x_i V_i = \sum_{i=1}^n x_i M_i / \rho_i \quad (16)$$

Where

x_i , M_i , and ρ_i address the mole division, molar mass, and thickness, separately, of part I in the combination and n is the quantity of parts in the blend. The isentropic compressibility for an ideal combination was assessed

utilizing the articulation proposed by Benson and Kiyohara^[27]. Overabundance sizes of the ternary frameworks were corresponded utilizing the Redlich and Kister articulation:

$$Q_{ij}^E = x_i x_j \sum_{\alpha=0}^p A_{\alpha} (2x_i - 1)^{\alpha} \quad (17)$$

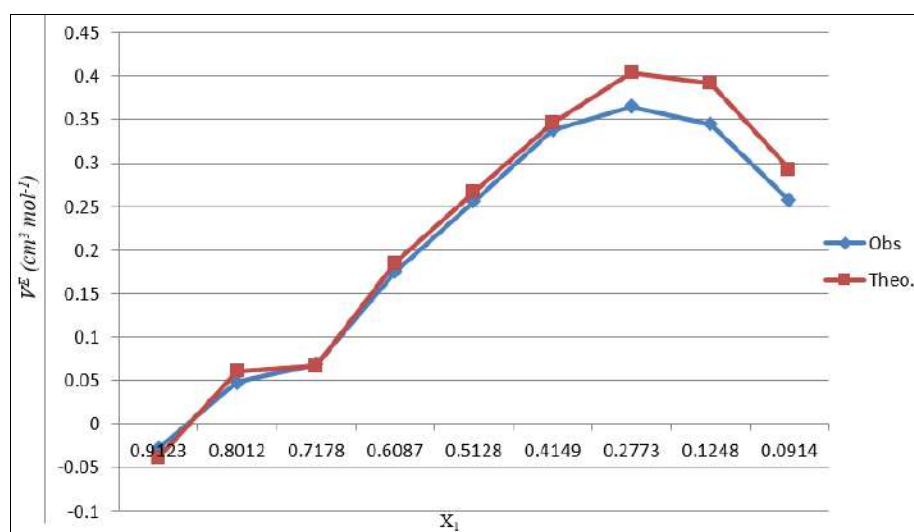


Fig 1: Excess molar volumes, V^E , of the ternary blends framed by the expansion of 1-Hexanol ($x_3=0.90-0.099$) to the parallel combinations of Cyclohexane + n-Heptane at 298.15 K

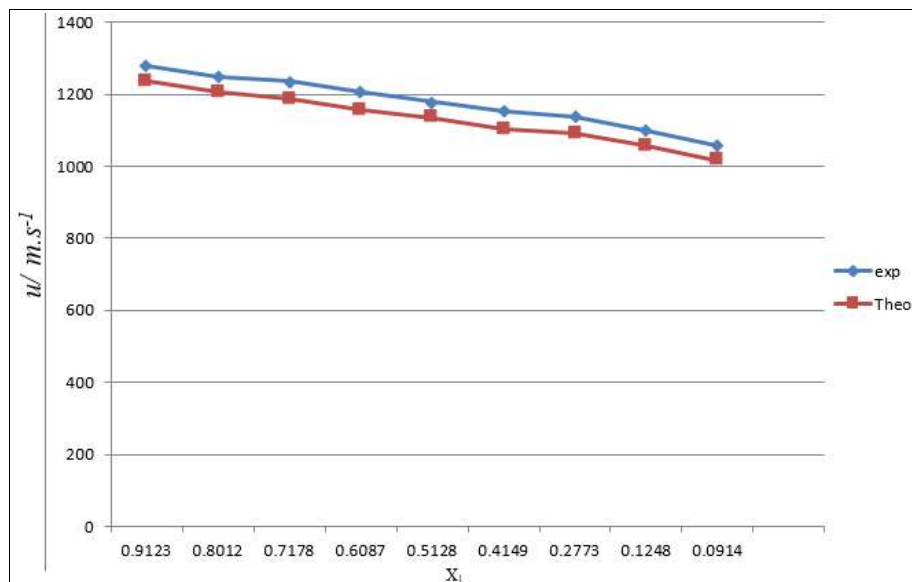


Fig 2: Experimental and hypothetical speed of sound, u_{Exp} u_{Theo} , of ternary combinations framed by the expansion of 1- Hexanol ($x_3= 0.90 - 0.099$) to the double combinations of Cyclohexane +n- Heptane at 298.15 K

Where x_i and x_j are the mole parts of the parts and A_p addresses the flexible fitting boundaries. An unweighted least-squares technique was utilized to compute these boundaries. The quantity of boundaries, m , was resolved utilizing the streamlining test. The upsides of the not entirely settled by numerous relapse investigation in light of the least squares strategy, and are summed up alongside the standard deviations between the test and fitted upsides of the separate capacity (Table 2). For abundance volume, the standard deviation ($\Delta\delta$) was 7×10^{-3} and 0.9 for overabundance isentropic compressibility's (Table 2). Table 3 records the information for the fluid blends. The upsides of such properties in the table fluctuated with the place of hydroxyl gathering of the alkanol. The clarifications of these outcomes was connected with an abatement of the affiliation power when the hydroxyl bunch is situated in a non essential position. As the mole part of alkanol diminishes, the worth of thickness and speed of sound reductions. On the other hand, the upsides of overabundance molar volume, V^E , isentropic compressibility, β_s and abundance isentropic compressibility, β^E increments with the reduction of mole part of alkanol. Table 3 records the information for the fluid blends. The upsides of such properties in the table fluctuated with the place of Plot of abundance molar volumes, V^E , for the ternary combinations framed by the expansion of 1-Hexanol ($x_3= 0.90 - 0.099$) to the twofold combinations of Cyclohexane + n-Heptane at 298.15 K with the mole division, x_1 is portrayed as Fig. 1. The overabundance volume can be deciphered in three regions, to be specific physical, synthetic and underlying impacts. The actual commitments containing scattering powers and vague physical (frail) communications, and the compound commitments include separating of the partners present in the unadulterated fluids, bringing about sure V^E values. The primary impacts emerges because of explicit associations, for example, arrangement of H-holding, charge - move (giver acceptor) edifices, and solid dipole-dipole communications between the part particles of the blend were bringing about regrettable V^E values. In present examination actual impacts are winning in every one of the ternary blends besides in couple of spots. Then again, compound and underlying impacts are contending with one

another to fluctuating degrees in the combinations. Fig.1 shows, the upsides of overabundance molar volumes, V^E , are positive besides in couple of spots demonstrating atomic relationship among hydroxyl and alkane particle coming about the development of hydrogen bond and show the frail connections between the parts because of pressing impact and dipolar-dipolar cooperation's. Conversely, negative qualities are a consequence of solid cooperation's between the part fluids. For positive deviations self-relationship of atoms is more predominant than pressing impact. Then again, for negative deviations, the pressing impact and dipolar-dipolar communications are more predominant than other impact. The real sign and greatness of deviations rely on the overall strength of these two contradicting impacts. A plot of trial and hypothetical speed of sound is developed and recorded as Fig.2. It is clear from Fig.2 that upsides of trial and hypothetical speed of sound are positive over the entire arrangement reach and increment with the increment of mole part of 1-Hexanol. The figured $\Delta\beta_T$ values demonstrate self-relationship of the alkanols with cyclic and n- alkanes because of its higher steric obstruction gives an upgrade of the obliteration of the liquor structure by the alkane particle, which suggests higher $\Delta\beta_T$. Physical (feeble) connections, and the substance commitments include separating of the partners present in the unadulterated fluids, bringing about certain V^E values. The underlying impacts emerges because of explicit communications, for example, arrangement of H-holding and solid dipole-dipole collaborations between the part particles of the combination, were bringing about regrettable V^E values. Positive upsides of abundance molar volumes (Fig.1) demonstrating atomic relationship among hydroxyl and alkane particle coming about the arrangement of hydrogen bond and show the feeble collaborations between the parts because of pressing impact. On the other hand, negative qualities are a consequence of solid cooperations between the part fluids. The registered $\Delta\beta_T$ values demonstrate self-relationship of the alkanols with cyclic and n-alkanes because of its higher steric obstruction gives an improvement of the annihilation of the liquor structure by the alkane atom, which suggests higher $\Delta\beta_T$.

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