

Ultrasonic study of molecular interaction in binary liquid mixtures of n-hexane with alcohols

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ABSTRACT

Ultrasonic velocity, viscosity and density of alcohol[s] in n-hexane have been measured at various temperatures in the range of 303.15 - 318.15K. From the experimental data, the acoustical parameters such as molar volume, adiabatic compressibility, intermolecular free length and their excess values have been computed and presented as functions of compositions. The deviations from ideality of the acoustical parameters are explained on the basis of molecular interactions between the components of the mixtures. The variations of these parameters with composition of the mixture suggest the strength of interactions in these mixtures.

Keyword:

n-hexane; alcohol; acoustical parameters; mixtures

1. INTRODUCTION

The liquid mixtures containing two or more liquids are ideal when there is no volume or enthalpy change on mixing. However, in actual practice, mixtures of liquids are not ideal. The deviation from ideality is explained on the basis of molecular interaction between the components of liquid mixtures. The study of intermolecular interaction has attracted the attention of many workers¹⁻¹⁰. The extensive investigation on liquid systems has been carried out by infrared, raman effect, magnetic susceptibility, nuclear magnetic resonance and ultrasonic methods. In recent years, ultrasonic technique has become a powerful tool in providing valuable information regarding the molecular behavior of liquids.

Excess properties are the measure of nonideality in liquid mixtures as a consequence of association or other types of interactions. The various types of molecular interactions that may operate between molecules of different types are dispersion forces, charge transfer, hydrogen bonding and dipole and dipole-induced dipole interactions. More than one type of interaction may be concerned in any given system. Dispersion forces, which are likely to be operative in every case, should make positive contribution to excess values. Charge transfer,

dipole-induced dipole and dipole-dipole interactions and hydrogen bonding between unlike components should make negative contributions. The magnitudes of the contributions made by these different types of interactions will vary with the components present and the composition of the mixture. Dissociation of a component, which is associated in the pure state, should make a positive contribution to excess values. The change from positive to increasingly negative excess values shows that the strength of the interaction between the components increases; this increase may be qualitatively interpreted in terms of closer approach of unlike molecules leading to reduction in compressibility and volume.

The knowledge of physicochemical properties of non-aqueous binary liquid mixtures has relevance in theoretical and applied areas of research, and such results are frequently used in design process (flow, mass transfer or heat transfer calculations) in many chemical and industrial processes¹¹. The excess properties derived from these physical property data reflect the physicochemical behavior of the liquid mixtures with respect to the solution structure and intermolecular interactions between the component molecules of the mixture¹²⁻¹⁴.

The variation of ultrasound velocities, adiabatic compressibilities and free volumes of binary liquid mixtures of protic, aprotic and associating liquids with changing mole fraction of one of the components has been investigated by earlier workers¹⁵⁻¹⁷. The trends of changes have been interpreted by these workers in terms of differences in size of the molecules and the strength of interactions taking place between the components of the mixtures. The non-ideal behaviour of liquid mixtures has been predicted by Tuomikoski and Numi¹⁸, Fort and Moore^{6,19}, Flory and Coworkers^{20,21}, Prakash *et al.*,^{22,23} and Raman and Naidu²⁴. The velocity of sound through liquid mixtures could be helpful in assessing the degree of association between the molecules^{25,26}. The molar sound velocity of non-associated liquids has been found to be independent, while that for associated liquid is dependent on temperature²⁷.

n-Hexane is a very good non-polar solvent. Alcohols are self-associated organic liquids and are widely used for the synthesis of other organic compounds. n-Propyl and iso-propyl alcohols are widely used as coupling and dispersing agents in the chemical, pharmaceutical and household industries and as carrier and extraction solvent for natural products. Branching of alkyl group attached to the hydroxyl group results in abnormal behaviour of alcohols.

The interaction of alcohol [s] with organic liquids is interesting due to its acidic nature. The O-H bonds in alcohols are polar and allow the release of the hydrogen atom as proton (H^+). The order of acidity in alcohols is : 1°-alcohol > 2°- alcohol > 3°-alcohol. This order is due to +I effect²⁸. While the interacting ability of alcohols is well established no such opinion is suggested from literature with regards to n-hexane. Keeping this in view, five binary liquid mixtures n-propyl alcohol, iso-propyl alcohol, n-butyl alcohol, sec-butyl alcohol and tert-butyl alcohol with n-hexane were selected to study their molecular interactions through their acoustical behaviour.

From the measured ultrasonic velocity, viscosity and density, the acoustical parameters such as molar volume, adiabatic compressibility, intermolecular free length and their excess values are computed for all the mixtures at various temperatures. The dependence of these parameters on composition has been used to explain the nature and extent of intermolecular interactions in these mixtures. The degree of association of alcohols in n-hexane is also calculated.

2. EXPERIMENTAL PROCEDURE

Ultrasonic velocity of pure liquids and liquid mixtures were measured at 3MHz with variable path single beam interferometer having gold plated quartz crystal at the bottom and double walled gold plated cell having grooves at inside walls to check the overlapping of stationary waves to produce clarity nodes and internodes. The accuracy of velocity measurements is $\pm 0.1 \text{ ms}^{-1}$. The densities of pure liquids and liquid mixtures were determined from the weight measurements on using the specific gravity bottle immersed in the thermostat at the experimental temperature and the accuracy in the measurements is $\pm 0.1 \text{ Kgm}^{-3}$. The viscosities of the mixtures were measured using an Ostwald's viscometer and were accurate to $\pm 0.001 \text{ Nsm}^{-2}$.

The liquids were of best available grade n-Hexane (BDH), n-propyl alcohol (BDH), iso-propyl alcohol (SD's fine chemicals), n-butyl alcohol (BDH), secondary butyl alcohol (E merck), tertiary butyl alcohol (BDH) and purified by standard methods described by Weissberger²⁹. The liquid mixtures were prepared by mixing calculated amount of pure liquids.

2. 1. Theory

From experimental data, the adiabatic compressibility, Molar volume, intermolecular free length³⁰ and their excess values were computed by the following relations.

$$\text{Molar volume, } V = M_{\text{eff}} / \rho$$

$$\text{Adiabatic compressibility, } \beta = 1 / u^2 \rho$$

$$\text{Intermolecular free length, } L_f = K \beta^{1/2}$$

Where M_{eff} is the effective molecular weight given by, $M_{\text{eff}} = x_1 M_1 + x_2 M_2$, M_1 and M_2 being the molecular weights, x_1 and x_2 are mole fractions of components 1 and 2, ρ is the density, u is the ultrasonic velocity, K is the temperature dependent Jacobson constant.

The excess values of all the parameters are computed by the expression,

$$A^E = A_{\text{exp}} - [x_1 A_1 + x_2 A_2]$$

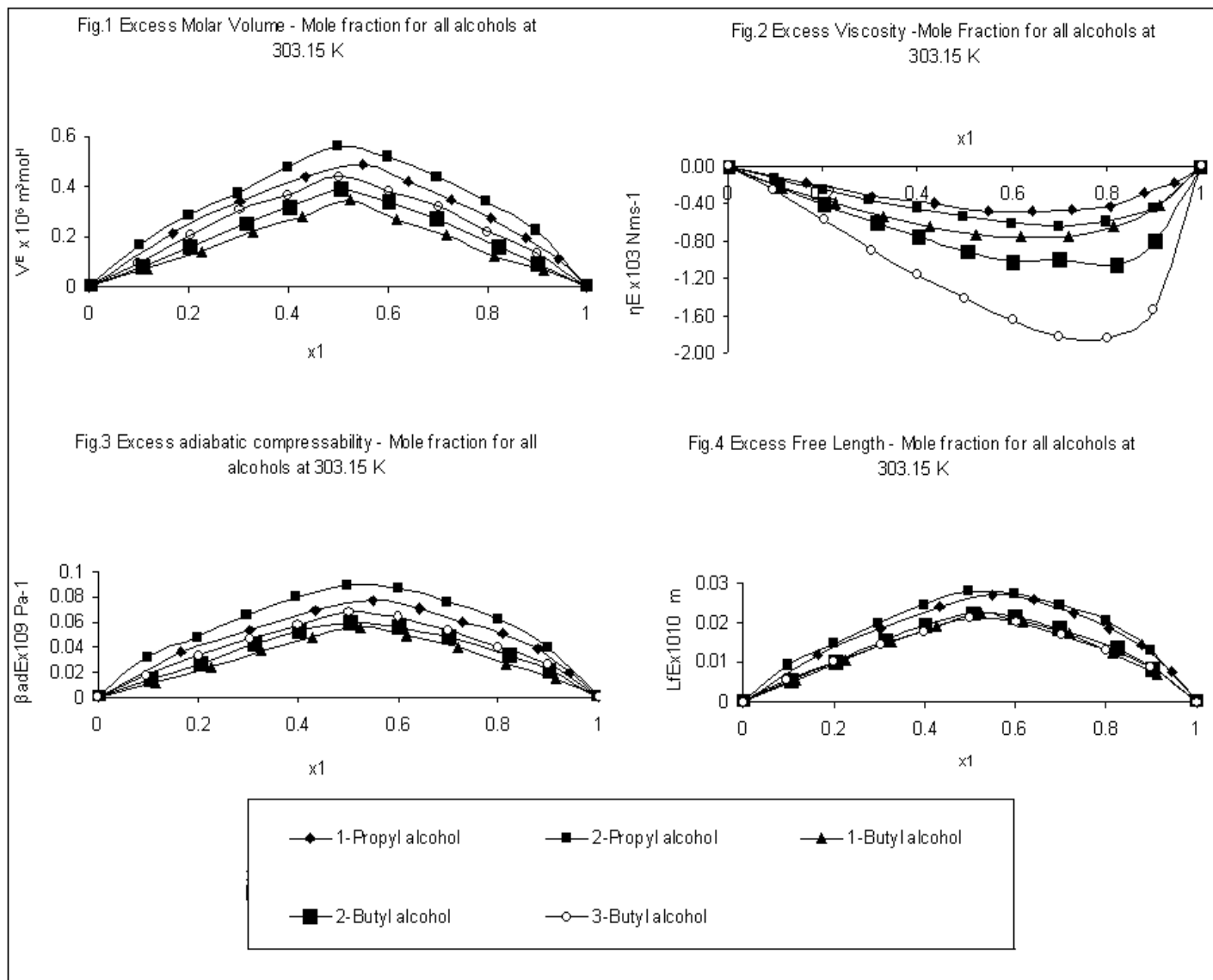
A represents various parameters, A^E being the excess value and A_{exp} the experimentally determined value.

3. RESULTS AND DISCUSSION

The experimental density, ultrasonic velocity, viscosity, the computed molar volume, adiabatic compressibility and free length data and their excess values for the alcohol [s] + n-hexane at various temperatures are given in Table 1 to 5. All the excess values of these parameters V^E , η^E , β^E and L_f^E at various temperatures are represented graphically in Fig. 1 to 4. The V^E , β^E and L_f^E are positive and η^E is negative for all the systems (n-Hexane + alcohol[s]) under study over the whole composition range of n-hexane (Fig. 1 to 4).

The positive values of V^E show that the interaction between alcohol[s] and n-hexane is weak, may be attributed to breaking of hydrogen bonds between alcohols. Prakash et al.³¹ observed that V^E are positive, involving the weak dispersion forces between molecules of dichloromethane and aromatic hydrocarbon molecules. This similar behaviour is also

observed by Aminabhavi and Gopalakrishna³² in the 2-ethoxy ethanol + n-Hexane system. The V^E values become more positive as the temperature is increased and they vary in the following order: n-butyl alcohol < sec-butyl alcohol < tert-butyl alcohol < n-propyl alcohol < iso-propyl alcohol. The behaviour of excess volumes with the mole fraction of alcohols for all the systems at 303.15K is shown in Fig.1.



The values of η^E are negative over the whole concentration range for all the mixtures at all temperatures (Fig.2) suggesting weak interaction between the components¹⁹. The η^E values increase with increasing chain length of alcohols³². The excess viscosities show a systematic decrease with increase of temperature (Table 1 to 5).

The excess adiabatic compressibilities are positive over the whole composition range for all mixtures at all the temperatures, indicating the breaking of hydrogen bonds³². The variation of excess adiabatic compressibility with the composition of alcohol[s] at 303.15K is given in Fig. 3. Such behaviour is also investigated by Venkatesulu et al³³ in trichloroethylene with 3-methyl-1-butanol, 2-butanol and 2-methyl-2-propanol. The study of

the adiabatic compressibility provides better understanding of the medium. The electrostatic field produced by the interacting atoms in the mixture influences the structural arrangement of molecules which in turn pronounces the effect of adiabatic compressibility. A negative value of adiabatic compressibility indicates strong interaction between the components of the mixture, while the positive values are indicative of weaker interaction³⁴. Gour et al.³⁵ pointed out that positive values in excess properties correspond mainly to the existence of dispersion forces.

The positive β^E values for hexane + alcohols systems follow the order: n-butyl alcohol < sec-butyl alcohol < tert-butyl alcohol < n-propyl alcohol < iso-propyl alcohol. This order shows that deviation in compressibility decreases with increased in chain length of the alcohol[s]. The excess free length values displayed in Fig.4, are positive for all the mixtures at all temperatures. Positive value of L_f^E indicates weak interaction, and this positive value is attributed to the molecular dissociation of an associated species caused by addition of an inert or an active solvent,

Table 1: Experimental Density (ρ), viscosity (η) and Ultrasonic Velocity (u) Data and Computed Parameters (V , β and L_f) and Their excess values for the n-Propyl alcohol (1) – n-Hexane (2) system at Different Temperature

Mole fraction x_1	ρ Kg m^{-3}	$\eta \times 10^3$ N $m s^{-1}$	u ms $^{-1}$	$V \times 10^6$ m $^3 mol^{-1}$	$\beta_{ad} \times 10^9$ Pa $^{-1}$	$L_f \times 10^{10}$ m	$\eta^E \times 10^3$ N $m s^{-1}$	$V^E \times 10^6$ m $^3 mol^{-1}$	$\beta_{ad}^E \times 10^9$ Pa $^{-1}$	$L_f^E \times 10^{10}$ m
1	2	3	4	5	6	7	8	9	10	11
303.15K										
0.0000	649.8	0.3139	1052.0	132.61	1.3906	0.7458	0.0000	0.0000	0.0000	0.0000
0.1664	663.7	0.3556	1059.9	123.30	1.3412	0.7325	-0.1751	0.2157	0.0354	0.0120
0.3032	677.1	0.3949	1070.0	115.59	1.2900	0.7183	-0.3140	0.3427	0.0539	0.0186
0.4344	691.9	0.4810	1080.2	108.17	1.2386	0.7039	-0.3988	0.4402	0.0694	0.0242
0.5499	707.0	0.5512	1091.1	101.60	1.1881	0.6894	-0.4791	0.4853	0.0777	0.0272
0.6409	721.1	0.6712	1105.2	96.32	1.1353	0.6739	-0.4776	0.4201	0.0713	0.0256
0.7274	736.1	0.7891	1121.3	91.30	1.0805	0.6574	-0.4724	0.3475	0.0605	0.0223
0.8070	751.5	0.9415	1136.8	86.66	1.0297	0.6418	-0.4237	0.2738	0.0502	0.0187
0.8770	766.6	1.1623	1152.3	82.57	0.9824	0.6269	-0.2941	0.1951	0.0387	0.0145
0.9427	782.3	1.3553	1171.9	78.73	0.9308	0.6102	-0.1867	0.1110	0.0205	0.0078
1.0000	797.7	1.6166	1192.8	75.33	0.8811	0.5937	0.0000	0.0000	0.0000	0.0000
308.15K										
0.0000	645.1	0.2980	1030.1	133.58	1.4609	0.7702	0.0000	0.0000	0.0000	0.0000
0.1664	658.9	0.3359	1038.2	124.20	1.4081	0.4561	-0.1479	0.2231	0.0372	0.0124
0.3032	672.1	0.3701	1048.2	116.45	1.3542	0.7415	-0.2665	0.3737	0.0574	0.0196
0.4344	686.8	0.4451	1059.3	108.97	1.2976	0.7258	-0.3380	0.4739	0.0719	0.0248
0.5499	701.9	0.5167	1071.3	102.34	1.2414	0.7099	-0.3954	0.5064	0.0782	0.0273
0.6409	715.9	0.6121	1084.9	97.02	1.1868	0.6942	-0.4016	0.4438	0.0729	0.0260
0.7274	730.9	0.7175	1100.8	91.95	1.1291	0.6771	-0.3928	0.3602	0.062	0.0227
0.8070	746.2	0.8612	1116.2	87.28	1.0756	0.6609	-0.3380	0.2885	0.0516	0.0191
0.8770	761.1	1.0166	1131.3	83.17	1.0266	0.6456	-0.2607	0.2227	0.0405	0.0150
0.9427	776.9	1.2091	1148.5	79.27	0.9758	0.6295	-0.1416	0.1189	0.0253	0.0093
1.0000	792.3	1.4147	1171.6	75.85	0.9195	0.6110	0.0000	0.0000	0.0000	0.0000
313.15K										
0.0000	641.0	0.2836	1010.0	134.43	1.5293	0.7939	0.0000	0.0000	0.0000	0.0000
0.1664	654.6	0.3178	1018.5	125.01	1.4727	0.7790	-0.1267	0.2610	0.0389	0.0129
0.3032	667.9	0.3510	1028.9	117.18	1.4143	0.7634	-0.2257	0.3909	0.0591	0.0201

0.4344	682.6	0.4137	1040.2	109.65	1.3539	0.7470	-0.2899	0.4898	0.0741	0.0254
0.5499	697.6	0.4839	1052.5	102.97	1.2940	0.7302	-0.3313	0.5356	0.0805	0.0280
0.6409	711.7	0.5600	1066.2	97.60	1.2360	0.7137	-0.3432	0.4566	0.0748	0.0266
0.7274	726.6	0.6560	1082.1	92.49	1.1754	0.6960	-0.3309	0.3844	0.0638	0.0232
0.8070	741.9	0.7860	1097.5	87.78	1.1190	0.6791	-0.2778	0.3111	0.0532	0.0196
0.8770	756.8	0.9810	1112.4	83.64	1.0678	0.6634	-0.1505	0.2441	0.0422	0.0155
0.9427	772.7	1.0752	1129.9	79.71	1.0137	0.6463	-0.1198	0.1288	0.0258	0.0095
1.0000	788.2	1.2504	1152.6	76.24	0.9550	0.6273	0.0000	0.0000	0.0000	0.0000
308.15K										
0.0000	638.5	0.2708	992.6	134.96	1.5896	0.8153	0.0000	0.0000	0.0000	0.0000
0.1664	651.9	0.3023	1000.8	125.53	1.5315	0.8003	-0.1091	0.2704	0.0417	0.0136
0.3032	665.0	0.3326	1011.5	117.69	1.4698	0.7840	-0.1944	0.4084	0.0620	0.0208
0.4344	679.5	0.3842	1023.0	110.15	1.4062	0.7669	-0.2537	0.5106	0.0771	0.0262
0.5499	694.3	0.4554	1035.8	103.46	1.3425	0.7493	-0.2801	0.5581	0.0826	0.0285
0.6409	708.2	0.5110	1049.5	98.08	1.2820	0.7322	-0.3014	0.4819	0.0767	0.0271
0.7274	722.9	0.6043	1065.1	92.96	1.2194	0.7141	-0.2812	0.4101	0.0660	0.0238
0.8070	738.1	0.7135	1080.2	88.24	1.1611	0.6968	-0.2393	0.3239	0.0555	0.0202
0.8770	752.8	0.8157	1095.1	84.09	1.1077	0.6806	-0.1963	0.2570	0.0440	0.0161
0.9427	768.6	0.9581	1112.9	80.13	1.0505	0.6628	-0.1094	0.1296	0.0262	0.0095
1.0000	783.9	1.1159	1135.2	76.66	0.9899	0.6434	0.0000	0.0000	0.0000	0.0000

Table 2: Experimental Density (ρ), viscosity (η) and Ultrasonic Velocity (u) Data and Computed Parameters (V , β and L_f) and Their excess values for the iso-Propyl alcohol (1) – n-Hexane (2) system at Different Temperatures.

Mole fraction x_1	ρ Kgm ⁻³	$\eta \times 10^3$ Nms ⁻¹	U ms ⁻¹	$V \times 10^6$ m ³ mol ⁻¹	$\beta_{ad} \times 10^9$ Pa ⁻¹	$L_f \times 10^{10}$ m	$\eta^E \times 10^3$ Nms ⁻¹	$V^E \times 10^6$ m ³ mol ⁻¹	$\beta_{ad}^E \times 10^9$ Pa ⁻¹	$L_f^E \times 10^{10}$ m
1	2	3	4	5	6	7	8	9	10	11
303.15K										
0.0000	649.8	0.3139	1052.0	132.61	1.3906	0.7458	0.0000	0.0000	0.0000	0.0000
0.0993	656.7	0.3346	1049.2	127.28	1.3833	0.7439	-0.1177	0.1637	0.0315	0.0093
0.1994	664.5	0.3490	1051.5	121.85	1.3611	0.7379	-0.2428	0.2860	0.0483	0.0146
0.2983	673.1	0.3732	1053.2	116.47	1.3394	0.7319	-0.3565	0.3756	0.0652	0.0199
0.3977	682.5	0.4150	1055.3	111.06	1.3157	0.7254	-0.5433	0.4794	0.0803	0.0247
0.4980	693.1	0.4730	1059.3	105.59	1.2858	0.7172	-0.5351	0.5628	0.0895	0.0277
0.5994	705.9	0.5480	1067.3	99.93	1.2436	0.7053	-0.6014	0.5188	0.0870	0.0274
0.6980	720.1	0.6445	1078.1	94.39	1.1948	0.6913	-0.6423	0.4391	0.0766	0.0246
0.7982	736.5	0.8359	1090.3	88.74	1.1422	0.6759	-0.5906	0.3396	0.0631	0.0205
0.8971	755.0	1.1239	1107.1	83.15	1.0806	0.6575	-0.4405	0.2273	0.0402	0.0132
1.0000	778.2	1.7078	1133.4	77.22	1.0003	0.6326	0.0000	0.0000	0.0000	0.0000
308.15K										
0.0000	645.1	0.2980	1030.1	133.58	1.4609	0.7702	0.0000	0.0000	0.0000	0.0000
0.0993	651.9	0.3188	1027.8	128.21	1.4521	0.7678	-0.1139	0.1840	0.0321	0.0094
0.1994	659.7	0.3319	1030.0	122.74	1.4288	0.7617	-0.2366	0.3055	0.0501	0.0149
0.2983	668.3	0.3532	1032.0	117.30	1.4050	0.7553	-0.3495	0.3942	0.0670	0.0202
0.3977	677.7	0.3850	1035.8	111.85	1.3753	0.7473	-0.4526	0.4975	0.0783	0.0239
0.4980	688.3	0.4458	1038.2	106.33	1.3479	0.7398	-0.5279	0.5805	0.0922	0.0282
0.5994	701.1	0.5007	1046.5	100.61	1.3024	0.7272	-0.6106	0.5347	0.0884	0.0275
0.6980	715.3	0.5951	1056.6	95.02	1.2522	0.7131	-0.6499	0.4532	0.0789	0.0249
0.7982	731.7	0.7483	1069.1	89.32	1.1957	0.6968	-0.6327	0.3522	0.0637	0.0204
0.8971	750.2	0.9800	1082.0	83.68	1.1386	0.6799	-0.5352	0.2390	0.0473	0.0152

1.0000	773.5	1.6548	1110.2	77.69	1.0489	0.6526	0.0000	0.0000	0.0000	0.0000
313.15K										
0.0000	641.0	0.2836	1010.0	134.43	1.5293	0.7939	0.0000	0.0000	0.0000	0.0000
0.0993	647.7	0.3035	1008.2	129.05	1.5189	0.7912	-0.0932	0.2188	0.0333	0.0096
0.1994	655.5	0.3155	1010.5	123.53	1.4940	0.7846	-0.1952	0.3537	0.0524	0.0155
0.2983	664.2	0.3356	1013.0	118.03	1.4672	0.7776	-0.2877	0.4375	0.0690	0.0206
0.3977	673.8	0.3595	1017.0	112.50	1.4349	0.7690	-0.3770	0.5221	0.0804	0.0243
0.4980	684.5	0.4212	1019.8	106.92	1.4047	0.7608	-0.4295	0.6063	0.0943	0.0286
0.5994	697.5	0.4584	1028.1	101.13	1.3564	0.7476	-0.5077	0.5485	0.0905	0.0279
0.6980	711.9	0.5504	1038.2	95.48	1.3032	0.7328	-0.5280	0.4590	0.0807	0.0253
0.7982	728.4	0.6718	1050.6	89.73	1.2438	0.7159	-0.5207	0.3672	0.0653	0.0208
0.8971	747.1	0.8632	1063.5	84.03	1.1834	0.6983	-0.4419	0.2541	0.0484	0.0155
1.0000	770.8	1.4223	1091.1	77.96	1.0898	0.6701	0.0000	0.0000	0.0000	0.0000
308.15k										
0.0000	638.5	0.2708	992.6	134.96	1.5896	0.8153	0.0000	0.0000	0.0000	0.0000
0.0993	645.1	0.2886	990.8	129.57	1.5791	0.8126	-0.0606	0.2275	0.0341	0.0097
0.1994	652.8	0.2995	993.0	134.04	1.5535	0.8060	-0.1288	0.3682	0.0535	0.0156
0.2983	661.4	0.3211	995.5	118.53	1.5256	0.7988	-0.1853	0.4557	0.0701	0.0206
0.3977	670.9	0.3375	999.3	112.98	1.4926	0.7901	-0.2474	0.5418	0.0817	0.0244
0.4980	681.5	0.4001	1002.1	107.39	1.4612	0.7817	-0.2641	0.6255	0.0954	0.0285
0.5994	694.4	0.4255	1009.8	101.59	1.4123	0.7685	-0.3188	0.5638	0.0920	0.0280
0.6980	708.6	0.5105	1019.5	95.92	1.3578	0.7535	-0.3117	0.4822	0.0818	0.0253
0.7982	724.9	0.6038	1030.8	90.16	1.2983	0.7369	-0.2975	0.3941	0.0673	0.0211
0.8971	743.5	0.7678	1043.2	84.44	1.2359	0.7189	-0.2116	0.2695	0.0494	0.0155
1.0000	767.1	1.0607	1069.2	78.34	1.1403	0.6903	0.0000	0.0000	0.0000	0.0000

Table 3: Experimental Density (ρ), viscosity (η) and Ultrasonic Velocity (u) Data and Computed Parameters (V , β and L_f) and Their excess values for the n-Butyl alcohol (1) – n-Hexane (2) system at Different Temperatures.

Mole fraction x_1	ρ Kgm ⁻³	$\eta \times 10^3$ Nms ⁻¹	U ms ⁻¹	$V \times 10^6$ m ³ mol ⁻¹	$\beta_{ad} \times 10^9$ Pa ⁻¹	$L_f \times 10^{10}$ m	$\eta^E \times 10^3$ Nms ⁻¹	$V^E \times 10^6$ m ³ mol ⁻¹	$\beta_{ad}^E \times 10^9$ Pa ⁻¹	$L_f^E \times 10^{10}$ m
1	2	3	4	5	6	7	8	9	10	11
303.15K										
0.0000	649.8	0.3139	1052.0	132.61	1.3906	0.7458	0.0000	0.0000	0.0000	0.0000
0.1152	662.1	0.3166	1062.3	128.05	1.3384	0.7317	-0.2254	0.0725	0.0124	0.0054
0.2261	674.8	0.3665	1072.5	123.66	1.2883	0.7179	-0.3951	0.1419	0.0246	0.0104
0.3271	687.1	0.4310	1081.5	119.68	1.2443	0.7055	-0.5306	0.2185	0.0372	0.0152
0.4270	700.2	0.5148	1091.4	119.72	1.1990	0.6925	-0.6446	0.2777	0.0479	0.0192
0.5231	713.6	0.6261	1102.3	111.92	1.1533	0.6792	-0.7236	0.3466	0.0562	0.0222
0.6171	728.6	0.7776	1120.3	108.06	1.0936	0.6614	-0.7582	0.2679	0.0491	0.0203
0.7182	745.8	0.9892	1142.3	103.94	1.0276	0.6411	-0.7468	0.2079	0.0399	0.0172
0.8143	763.7	0.2817	1167.2	99.98	0.9611	0.6200	-0.6446	0.1201	0.0273	0.0124
0.9124	783.2	0.7022	1195.2	95.99	0.8938	0.5979	-0.4183	0.0665	0.0151	0.0070
1.0000	802.2	2.2940	1225.8	92.40	0.8296	0.5761	0.0000	0.0000	0.0000	0.0000
308.15K										
0.0000	645.1	0.2980	1030.1	133.58	1.4509	0.7702	0.0000	0.0000	0.0000	0.0000
0.1152	657.3	0.2472	1040.3	128.99	1.4058	0.7555	-0.2483	0.0846	0.0132	0.0057
0.2261	669.9	0.3431	1050.9	124.57	1.3517	0.7408	-0.3425	0.1650	0.0248	0.0106
0.3271	682.2	0.4004	1060.2	120.54	1.3041	0.7277	-0.4583	0.2346	.0372	0.0153

0.4270	695.3	0.4741	1070.6	116.53	1.2548	0.7138	-0.5559	0.2871	0.0471	0.0190
0.5231	708.7	0.5660	1082.0	112.70	1.2053	0.6995	-0.6288	0.3504	0.0546	0.0217
0.6171	723.6	0.7023	1100.0	108.81	1.1421	0.6810	-0.6536	0.2799	0.0472	0.0198
0.7182	740.8	0.8762	1122.1	104.64	1.0721	0.6598	-0.6530	0.2126	0.0371	0.0164
0.8143	758.6	1.1719	1146.5	100.66	1.0029	0.6381	-0.5221	0.1315	0.0249	0.0117
0.9124	778.1	1.4311	1175.1	96.61	0.9307	0.6147	-0.4310	0.0715	0.0109	0.0056
1.0000	792.1	2.0123	1202.3	92.99	0.8679	0.5936	0.0000	0.0000	0.0000	0.0000
313.15K										
0.0000	641.0	0.2836	1010.0	134.43	1.5293	0.7939	0.0000	0.0000	0.0000	0.0000
0.1152	653.1	0.2271	1020.0	129.82	1.4717	0.7788	-0.2283	0.0933	0.0144	0.0060
0.2261	665.6	0.3200	1030.9	125.37	1.4137	0.7633	-0.3008	0.1812	0.0257	0.0109
0.3271	677.8	0.3658	1040.0	121.32	1.3641	0.7497	-0.4056	0.2579	0.0392	0.0159
0.4270	690.7	0.4354	1051.0	117.31	1.3107	0.7349	-0.4580	0.3331	0.0483	0.0194
0.5231	704.2	0.5186	1062.3	113.42	1.2584	0.7201	-0.5452	0.3684	0.0561	0.0222
0.6171	718.9	0.6416	1080.1	109.52	1.1923	0.7010	-0.5623	0.3165	0.0488	0.0203
0.7182	736.1	0.7733	1102.0	105.31	1.1187	0.6790	-0.5814	0.2354	0.0383	0.0169
0.8143	753.9	1.0480	1126.1	101.28	1.0460	0.6565	-0.4500	0.1416	0.0258	0.0121
0.9124	773.3	1.2535	1154.2	97.21	0.9707	0.6325	-0.3909	0.0824	0.0118	0.0060
1.0000	792.3	1.7750	1181.5	93.55	0.9042	0.6104	0.0000	0.0000	0.0000	0.0000
308.15K										
0.0000	638.5	0.2708	992.6	134.96	1.5896	0.8153	0.0000	0.0000	0.0000	0.0000
0.1152	650.3	0.2095	1002.1	130.38	1.5313	0.8002	-0.2111	0.1166	0.0162	0.0065
0.2261	662.6	0.2997	1013.1	125.94	1.4704	0.7842	-0.2651	0.2044	0.0270	0.0112
0.3271	674.7	0.3392	1022.1	121.88	1.4187	0.7703	-0.3570	0.2628	0.0406	0.0162
0.4270	687.3	0.3975	1033.2	117.89	1.3630	0.7550	-0.4286	0.3530	0.0494	0.0196
0.5231	700.6	0.4778	1044.2	114.00	1.3091	0.7399	-0.4737	0.3831	0.0576	0.0225
0.6171	715.1	0.5783	1061.5	110.10	1.2411	0.7204	-0.4950	0.3229	0.0503	0.0207
0.7182	732.0	0.6935	1083.0	105.90	1.1647	0.6979	-0.5112	0.2416	0.0394	0.0171
0.8143	749.4	0.9293	1106.5	101.89	1.0899	0.6751	-0.4004	0.1585	0.0266	0.0123
0.9124	768.5	1.1153	1133.5	97.82	1.0128	0.6508	-0.3420	0.0905	0.0129	0.0063
1.0000	787.2	1.5712	1160.5	94.16	0.9432	0.6281	0.0000	0.0000	0.0000	0.0000

Table 4: Experimental Density (ρ), viscosity (η) and Ultrasonic Velocity (u) Data and Computed Parameters (V , β and L_f) and Their excess values for the sec-Butyl alcohol (1) – n-Hexane (2) system at Different Temperature.

Mole fraction x_1	ρ Kgm ⁻³	$\eta \times 10^3$ Nms ⁻¹	U ms ⁻¹	$V \times 10^6$ m ³ mol ⁻¹	$\beta_{ad} \times 10^9$ Pa ⁻¹	$L_f \times 10^{10}$ m	$\eta^E \times 10^3$ Nms ⁻¹	$V^E \times 10^6$ m ³ mol ⁻¹	$\beta_{ad}^E \times 10^9$ Pa ⁻¹	$L_f^E \times 10^{10}$ m
1	2	3	4	5	6	7	8	9	10	11
303.15K										
0.0000	649.8	0.3139	1052.0	132.61	1.3906	0.7458	0.0000	0.0000	0.0000	0.0000
0.1051	660.7	0.3340	1058.6	128.51	1.3506	0.7350	-0.2112	0.0805	0.0144	0.0055
0.2041	671.6	0.3603	1065.4	124.65	1.3118	0.7244	-0.4027	0.1609	0.0269	0.0102
0.3141	684.5	0.3923	1072.5	120.36	1.2701	0.7128	-0.6128	0.2557	0.0421	0.0156
0.4023	695.6	0.4422	1078.9	116.91	1.2350	0.7029	-0.7570	0.3193	0.0527	0.0194
0.5058	709.5	0.5097	1088.6	112.86	1.1894	0.6897	-0.9172	0.3925	0.0606	0.0223
0.5999	723.8	0.6224	1102.5	109.07	1.1366	0.6743	-1.0116	0.3433	0.0566	0.0214
0.6989	740.1	0.8449	1120.3	105.05	1.0766	0.6562	-1.0069	0.2717	0.0478	0.0187
0.8222	762.4	1.0769	1146.5	100.03	0.9979	0.6318	-1.0463	0.1601	0.0330	0.0134
0.9004	777.7	1.4936	1166.4	96.85	0.9451	0.6149	-0.8016	0.0945	0.0207	0.0086

1.0000	798.8	2.5144	1197.6	92.79	0.8728	0.5909	0.0000	0.0000	0.0000	0.0000
308.15K										
0.0000	645.1	0.2980	1030.1	133.58	1.4609	0.7702	0.0000	0.0000	0.0000	0.0000
0.1051	656.0	0.3192	1036.5	129.43	1.4189	0.7590	-0.1674	0.0888	0.0161	0.0060
0.2041	666.9	0.3414	1043.6	125.52	1.3768	0.7477	-0.3228	0.1774	0.0288	0.0108
0.3141	679.9	0.3664	1051.8	121.17	1.3295	0.7347	-0.4951	0.2643	0.0423	0.0158
0.4023	691.0	0.4147	1058.9	117.69	1.2907	0.7239	-0.6051	0.3370	0.0522	0.0193
0.5058	704.9	0.4729	1068.5	113.60	1.2426	0.7103	-0.7326	0.4213	0.0614	0.0226
0.5999	719.3	0.5641	1082.5	109.75	1.1864	0.6941	-0.8102	0.3660	0.0572	0.0217
0.6989	735.7	0.7230	1100.2	105.68	1.1229	0.6752	-0.8289	0.2909	0.0485	0.0190
0.8222	758.2	0.9248	1126.1	100.58	1.0401	0.6498	-0.8483	0.1681	0.0338	0.0137
0.9004	773.6	1.2900	1146	97.36	0.9843	0.6322	-0.6234	0.1017	0.0212	0.0088
1.0000	794.9	2.0921	1177.1	93.24	0.9079	0.6072	0.0000	0.0000	0.0000	0.0000
313.15K										
0.0000	641.0	0.2836	1010.0	134.43	1.5293	0.7939	0.0000	0.0000	0.0000	0.0000
0.1051	651.8	0.3051	1016.2	130.26	1.4857	0.7825	-0.1350	0.1111	0.0182	0.0066
0.2041	662.7	0.3240	1023.8	126.32	1.4396	0.7702	-0.2634	0.2015	0.0304	0.0113
0.3141	675.7	0.3476	1032.8	121.93	1.3874	0.7561	-0.4036	0.2908	0.0430	0.0161
0.4023	686.8	0.3890	1040.1	118.41	1.3459	0.7447	-0.4935	0.3658	0.0534	0.0198
0.5058	700.8	0.4399	1049.9	114.26	1.2945	0.7304	-0.5966	0.4371	0.0629	0.0231
0.5999	715.2	0.5156	1064.0	110.38	1.2351	0.7134	-0.6610	0.3846	0.0588	0.0222
0.6989	731.6	0.6365	1082.1	106.27	1.1673	0.6936	-0.6875	0.3128	0.0493	0.0194
0.8222	754.2	0.8101	1107.9	101.12	1.0802	0.6672	-0.6974	0.1814	0.0347	0.0141
0.9004	769.6	1.1192	1127.8	97.87	1.0216	0.6488	-0.5047	0.1194	0.0221	0.0091
1.0000	791.1	1.7722	1159.1	93.69	0.9409	0.6227	0.0000	0.0000	0.0000	0.0000
308.15K										
0.0000	638.5	0.2708	992.6	134.96	1.5896	0.8153	0.0000	0.0000	0.0000	0.0000
0.1051	649.1	0.2912	998.1	130.80	1.5465	0.8042	-0.1089	0.1243	0.0209	0.0073
0.2041	659.8	0.3079	1006.0	126.88	1.4976	0.7914	-0.2139	0.2259	0.0324	0.0118
0.3141	672.6	0.3295	1015.1	122.49	1.4429	0.7768	-0.3276	0.3195	0.0448	0.0165
0.4023	683.6	0.3649	1022.6	118.96	1.3989	0.7649	-0.4007	0.385	0.0546	0.0200
0.5058	697.4	0.4086	1032.2	114.82	1.3458	0.7502	-0.4843	0.4469	0.0646	0.0235
0.5999	711.6	0.4733	1045.9	110.94	1.2846	0.7330	-0.5353	0.4036	0.0608	0.0227
0.6989	727.8	0.5794	1063.5	106.83	1.2148	0.7128	-0.5510	0.3265	0.0513	0.0199
0.8222	750.0	0.7205	1089.2	101.68	1.1239	0.6856	-0.5615	0.2035	0.0356	0.0143
0.9004	765.3	0.9771	1108.4	98.42	1.0636	0.6669	-0.4011	0.1234	0.023	0.0093
1.0000	786.5	1.5007	1139.1	94.24	0.9799	0.6402	0.0000	0.0000	0.0000	0.0000

Table 5: Experimental Density (ρ), viscosity (η) and Ultrasonic Velocity (u) Data and Computed Parameters (V , β and L_f) and Their excess values for the tert-Butyl alcohol (1) – n-Hexane (2) system at Different Temperatures.

Mole fraction x_1	ρ Kgm^{-3}	$\eta \times 10^3$ Nms^{-1}	U ms^{-1}	$V \times 10^6$ $\text{m}^3 \text{mol}^{-1}$	$\beta_{ad} \times 10^9$ Pa^{-1}	$L_f \times 10^{10}$ m	$\eta^E \times 10^3$ Nms^{-1}	$V^E \times 10^6$ $\text{m}^3 \text{mol}^{-1}$	$\beta_{ad}^E \times 10^9$ Pa^{-1}	$L_f^E \times 10^{10}$ m
1	2	3	4	5	6	7	8	9	10	11
303.15K										
0.0000	649.8	0.3139	1052.0	132.61	1.3906	0.7458	0.0000	0.0000	0.0000	0.0000
0.0952	658.2	0.3567	1050.9	121.18	1.3757	0.7418	-0.2575	0.0914	0.0177	0.0054
0.2011	668	0.371	1051.2	125.37	1.3547	0.7361	-0.5771	0.2091	0.0329	0.0101
0.3031	678.1	0.3849	1051.8	121.69	1.3330	0.7302	-0.8849	0.3078	0.0461	0.0142
0.3994	688.4	0.4218	1052.5	118.18	1.3113	0.7242	-1.1518	0.3689	0.0574	0.0177

0.5008	699.9	0.4769	1053.4	114.50	1.2876	0.7177	-1.4165	0.4376	0.0683	0.0210
0.6007	712.8	0.5643	1059.6	110.74	1.2495	0.7070	-1.6441	0.3775	0.0644	0.0202
0.6999	726.5	0.7084	1069.2	107.00	1.2041	0.6940	-1.8129	0.3189	0.0529	0.0169
0.7999	741.6	0.9908	1079.3	103.20	1.1576	0.6805	-1.8459	0.2199	0.0406	0.0132
0.8988	757.6	1.6081	1090.3	99.45	1.1104	0.6664	-1.5405	0.1312	0.0273	0.0089
1.0000	775.6	3.4678	1108.9	95.56	1.0485	0.6476	0.0000	0.0000	0.0000	0.0000
					308.15K					
0.0000	645.1	0.2980	1030.1	133.58	1.4609	0.7702	0.0000	0.0000	0.0000	0.0000
0.0952	653.4	0.3370	1028.5	130.13	1.4468	0.7664	-0.1893	0.1131	0.0204	0.0060
0.2011	663.3	0.3488	1029.0	126.26	1.4238	0.7603	-0.4314	0.2134	0.0359	0.0108
0.3031	673.4	0.3626	1030.2	122.54	1.3992	0.7537	-0.6622	0.3148	0.0482	0.0146
0.3994	683.6	0.3943	1031.5	119.01	1.3749	0.7471	-0.8614	0.3957	0.0588	0.0179
0.5008	695.1	0.4466	1032.9	115.29	1.3485	0.7399	-1.0523	0.4666	0.0692	0.0211
0.6007	708.0	0.5196	1038.5	111.49	1.3096	0.7292	-1.2188	0.4074	0.0666	0.0206
0.6999	721.7	0.6381	1048.2	107.71	1.2611	0.7156	-1.3382	0.3502	0.0541	0.0171
0.7999	736.8	0.857.0	1057.9	103.87	1.2127	0.7017	-1.3591	0.2527	0.0419	0.0135
0.8988	753.0	1.3352	1068.5	100.05	1.1632	0.6872	-1.118	0.1396	0.0283	0.0091
1.0000	771.1	2.6959	1086.7	96.12	1.0982	0.6677	0.0000	0.0000	0.0000	0.0000
					313.15K					
0.0000	641.0	0.2836	1010.0	134.43	0.5293	0.7939	0.0000	0.0000	0.0000	0.0000
0.0952	649.2	0.3196	1008.6	130.97	1.5142	0.7899	-0.1403	0.1318	0.0212	0.0062
0.2011	659.0	0.3291	1009.2	127.08	1.4899	0.7836	-0.3269	0.2488	0.0373	0.0111
0.3031	669.1	0.3429	1010.7	123.33	1.4631	0.7765	-0.5020	0.3473	0.0494	0.0148
0.3994	679.3	0.3702	1011.9	119.77	1.4377	0.7697	-0.6530	0.4256	0.0608	0.0182
0.5008	690.8	0.4179	1013.8	116.01	1.4085	0.7618	-0.7931	0.4941	0.0703	0.0211
0.6007	703.7	0.4788	1019.2	112.17	1.3680	0.7508	-0.9172	0.4313	0.0680	0.0207
0.6999	717.5	0.5793	1028.2	108.34	1.3183	0.7371	-1.0004	0.3559	0.0561	0.0175
0.7999	732.5	0.7593	1037.9	104.48	1.2673	0.7227	-1.0056	0.2704	0.0432	0.0137
0.8988	748.6	1.1135	1048.2	100.64	1.2158	0.7078	-0.8345	0.1680	0.0295	0.0094
1.0000	766.9	2.1354	1065.6	96.65	1.1477	0.6877	0.0000	0.0000	0.0000	0.0000
					308.15K					
0.0000	638.5	0.2708	992.6	134.96	1.5896	0.8153	0.0000	0.0000	0.0000	0.0000
0.0952	646.5	0.3039	991.2	131.52	1.5744	0.8114	-0.1065	0.1566	0.0221	0.0063
0.2011	656.2	0.3111	991.8	127.63	1.5492	0.8049	-0.2546	0.2738	0.0384	0.0112
0.3031	666.2	0.3247	993.1	123.87	1.5220	0.7978	-0.3905	0.3714	0.0511	0.0151
0.3994	676.3	0.3480	994.1	120.30	1.4953	0.7908	-0.5084	0.4485	0.0621	0.0184
0.5008	687.7	0.3908	996.1	116.53	1.4655	0.7829	-0.6143	0.5132	0.0720	0.0214
0.6007	700.4	0.4410	1001.3	112.70	1.4241	0.7717	-0.7105	0.4605	0.0697	0.0210
0.6999	714.2	0.5282	1009.7	108.84	1.3734	0.7579	-0.7688	0.3617	0.0579	0.0178
0.7999	729.0	0.6694	1019.1	104.98	1.3208	0.7432	-0.7742	0.2817	0.0444	0.0139
0.8988	744.9	0.9561	1028.9	101.14	1.2681	0.7282	-0.6325	0.1821	0.0305	0.0096
1.0000	763.1	1.737	1045.9	97.13	1.1979	0.7078	0.0000	0.0000	0.0000	0.0000

producing considerable deviation³⁶. If a polar liquid is diluted with a non-polar one, the dipole-induced dipole interactions between the polar molecules and non-polar molecules of the diluent should result in an additional increase in free length and also compressibility and a corresponding decrease in velocity. Such a situation is already discussed by Orzechowki and Ernst³⁷. The magnitude of excess free length values of n-propyl alcohol and iso-propyl alcohol are almost same and also for butanol [s] systems at all temperatures. So these value change according to the sequence butanol[s] < propanol[s]. The effect of temperature on the

excess free length is small for all the system. Similar results are observed for this type (polar – nonpolar) of binary liquid mixtures^{38,39}.

Most of the β^E , L_f^E and V^E are positive and η^E are found to be negative in these systems indicating weak interactions between the components of mixtures⁴⁰. Such weakly interacting components are already investigated by earlier workers⁴¹⁻⁴³. Dispersion forces are responsible for positive deviations. The observed values of these parameters indicate that dissociation of the alcohol aggregates predominates over association between unlike molecules. If a polar liquid is diluted with non-polar one, the dipole – induced dipole interaction takes place between the molecules⁴⁴. The Vander waal type of interactions are present in hexane, while alcohols are polar and associate strongly through hydrogen bonding. In alcohols + n-hexane mixtures, the alcohol molecules associate in inert hexane medium and form clusters⁴⁵. There are molecular size holds or voids in such structures.

There is a considerable evidence to show that alcohols exist as closed ring structures as dimmers and trimers as shown in Diagram 1.

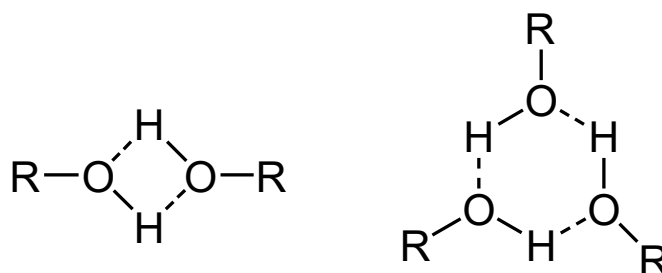


Diagram 1. Structural representation of dimmers and trimers.

Such a structural representation is already suggested in $\text{CCl}_4 + \text{Alcohol [s]}$ by Subharao and Gopalakrishnan⁴⁵. The addition of small quantity of passive diluent is usually to get into the interstices and causing a small degree of breaking of hydrogen bonds between the molecules of the alcohols. However the n-hexane molecules have no such clustering tendency. As the concentration of the alcohol molecule increases, some of the hexane molecules go to fill the voids in the alcohol structure.

4. CONCLUSION

The ultrasonic velocity, adiabatic compressibility, free length and viscosity with the mole fraction of alcohol for all the systems vary regularly without showing any maxima or minima and thereby corroborating the non existence of any complex formation. Same trend is seen at all the temperatures. In these systems, the magnitude of the excess acoustical parameters values are inferred only the weak interaction between alcohol [s] and n-Hexane molecule. This weak interaction may be due to rupture of hydrogen bonds via dissociation or dilution takes between the alcohol molecules.

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