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Studies of Ultrasonic Velocity, Viscosity and Density of Binary System of T-Butyl Alcohol, N-Butyl Alcohol and Iso-Pentyl Alcohol with O-Nitrotulune at 298.15 and 308.15 K

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Abstract:-

The Ultrasonic velocity, Viscosity and Density of binary system of t-butyl alcohol, n-butyl alcohol and iso-pentyl alcohol with O-nitrotulune have been measured at 298.15K and 308.15 K. The measured data reported over entire range of mole fraction. The analysis of obtained calculated data gave information about parameters such as viscosity deviation ($\Delta\eta$), excess molar volume (V^E), deviation in isentropic compressibility (ΔK_S) ,Excess free length (L_f^E), Internal pressure (π^E) ,available volume (V_a^E) and Gibbs free energy(G^{*E}) of binary system from these data attribute the intermolecular interaction between alcohols and O-nitrotolune solvent. The observed parameters and their changes well correlate to each other.

Key word:– Ultrasonic velocity, Viscosity, Density, Excess molar volume (V^E), Viscosity deviation ($\Delta\eta$) ,Excess free length (L_f^E), Excess internal pressure (π^E)

Introduction:–

Liquid mixture is used in product formulation and processing system in many industrial applications rather than single liquid component system. There are different physical methods like ultrasonic velocity, viscosity, density measurements to identify the strength of intermolecular interactions in the binary solutions (1,2). The intermolecular free length and internal pressure is an important physical property of liquid mixture which mainly affects the ultrasonic velocity. (3,4).

In present research work the experimental values of ultrasonic velocity, viscosity and density of t-butyl alcohol, n-butyl alcohol and iso-pentyl alcohol with O-nitrotulune at 298.15 and 308.15K was reported(5,6). These data have been used to calculate various parameters. For present study solvent contain bulky groups like nitro group and methyl group on aromatic benzene ring. Due to high polarity of solvent the interaction between bulky groups and alcohol are not unusual. This study well interprets the volumetric, viscometric and ultrasound effect of solute and solvent. The point of interest is highly polar functional groups –OH and Nitro present in the selected solute (alkanols) and solvent (Nitro toluene)

Experimental –

The chemicals used are of A.R. grade with minimum assay of 99.9% obtained from Sigma Aldrich or s. d. fine chemicals India. Bi-capillary pycnometer (10ml) was used to measured densities. An airtight stopper bottles were used to prepare and store the binary liquid mixtures of different known concentrations. The shimatzu electronic digital balance (± 0.1mg.) was used to measured weights of the samples. The Ubbelohde viscometer (20ml) was used to

measure the viscosity. The efflux time was determined using a digital clock to within ±0.015sec. The ultrasonic velocities (U) in liquid mixtures were measured using an ultrasonic interferometer (Mittal, F-81, 2 MHz, ±0.1 ms^{-1}).

Theory and Calculation:

Following equations been used to calculate different parameters in binary solutions

a) The molar excess volume

$$V^E = \frac{M_1X_1+M_2X_2}{\rho_{12}} - \frac{M_1X_1}{\rho_1} - \frac{M_2X_2}{\rho_2} \quad (1)$$

b) The viscosity deviation

$$\ln\eta_m = X_1\ln\eta_1 + X_2\ln\eta_2 \quad (2)$$

$$\Delta\eta_m = \eta_{12} - X_1\eta_1 - X_1\eta_2 \quad (3)$$

c) Deviation in isentropic compressibility

$$\Delta k_S = k_S - \Phi_1 k_{S1} - \Phi_2 k_{S2} \quad (4)$$

Where k_{S1}, k_{S2} and k_S are isentropic compressibility of liquid mixtures and Φ is volume fraction of pure i^{th} component in the mixture and is defined as

$$\phi = \frac{(Xi\ Vi)}{(\Sigma\ Xi\ Vi)} \quad (5)$$

Where x_1 and V_i are mole fraction and molar volume of ith component in the mixture.

d) The excess free length

$$L_f^E = L_{fmix} - x_1L_{f1} - x_2L_{f2} \quad (6)$$

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

Where $A_{id} = \sum Ai\ Xi$, Ai is any acoustical parameters and Xi the mole fraction of the liquid component.

e) Available volume

$$V_a = (V_m - V_0) = V_m(1 - U/U_m) \quad (8)$$

Where $V_m = M/\rho$, is the molar volume, U=Velocity, $V_0 = M/\rho_0$ = molar volume at absolute zero temperature and U_m = Schaaf's limiting value taken as 1600m/s for liquids.

f) The excess Gibbs free energy of flow

$$G^{*E} = RT[\ln(\eta V) - x_1\ln(\eta_1V_1) - x_2\ln(\eta_2V_2)] \quad (9)$$

Where V_i is the molar volume of ith component.

g) Internal pressure

$$\pi_i = bRT\,(K\,\square / U)^{1/2}\,(\square^{2/3} / M^{7/6}) \quad (10)$$

Where b is packing factor, K is a constant independent of temperature having value of 4.28×10^9, R is gas constant and M is molecular weight the other symbols have their usual meaning.

Result and Discussion:–

The measures values such as density (ρ), viscosity (η), ultrasonic velocity (U), viscosity deviation (Δη) , excess molar volume (V^E), deviation in isentropic compressibility (ΔK_S) ,are given in Table-1, Table-2 and Table-3 respectively while Excess free length(L_f^E), Internal pressure (π^E) ,available volume (V_a^E) and Gibbs free energy(G^{*E}) are given in Table-4, Table-5 and Table-6 respectively. Figure :- 1, a,b,c and d shows Ultrasonic velocity (U), Excess molar

volume (V^E), Viscosity deviation ($\Delta\eta$) and Deviation in isentropic compressibility (ΔK_S) against mole fraction for binary system of t-butyl alcohol, n-butyl alcohol, iso-pentyl alcohol at 298.15 K respectively.All these parameters shows negative deviations with minima at about X_2= 0.4-0.6. And Figure:-2, a,b,c and d shows Excess free length(L_f^E), Internal pressure (π^E),available volume (V_a^E) and Gibbs free energy(G^{*E}) against mole fraction for same solutions at same temperature these parameters except available volume are negative(7-9) this may be due to presence of stronger solute solvent interactions in between highly polar functional groups Nitro and -OH. This causes fitting of alkanol molecules in the voids of self associated nitro benzene solvent molecules resulting volume contraction than ideal(10,11). With increase in temperature all these parameters becomes less negative showing less salvation effect at higher temperature.

Summary:-

From experimental data ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for binary system at 298.15 and 308.15 K. The data have been used to compute the parameters $\Delta\eta$,V^E, ΔK_S, L_f^E, π^E , V_a^E and G^{*E}. It is a well justified that most of values are negative due to presence of polar functional groups on aromatic ring and alkanols which increases salvation effect in solution so it shows structure making interactions between solvent and solute.

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Table.1. Values of densities viscosities, ultrasonic velocity, Excess molar volumes and Deviation in viscosity and deviation in isentropic compressibility for binary system of t-butyl alcohol and O-nitrotolune at 298.15 and 308.15 K.

Temp K	X_1	ρ (gm /cm^3)	$\eta 10^3$ (Nsm^{-2})	U(MS^{-1})	$V^E x10^6$ (m^3/mole)	$\Delta \eta x10^3$ (Kg m^{-1}s^{-1})	$\Delta ksx10^{11}$ (m^{2}N^{-1})

298.15	0.0000	0.78100	4.44820	1373.6	0.0000	0.0000	0.00
	0.0570	0.80150	3.13530	1384.2	0.1512	-116.9779	4.76
	0.1194	0.83950	2.60270	1462.6	-1.6374	-154.5213	-55.64
	0.1882	0.87060	2.45480	1471.3	-2.4279	-151.9826	-46.03
	0.2649	0.89240	2.15450	1482.3	-1.9835	-162.6942	-28.59
	0.3510	0.93530	2.01440	1431.7	-3.7231	-155.0182	-23.58
	0.4480	0.97030	1.92940	1565.4	-4.3708	-139.0868	-34.27
	0.5578	0.97470	1.63650	1641.0	-5.4102	-140.7214	-28.01
	0.6836	0.98930	1.55990	1685.8	-7.7530	-116.6962	-4.21
	0.8294	1.02530	1.48000	1730.4	-8.6924	-87.9636	18.50
	1.0000	1.06920	1.92950	1932.0	0.0000	0.0000	0.00
308.15	0.0000	0.77240	2.66790	1311.7	0.0000	0.0000	0.00
	0.0570	0.79140	2.09330	1333.0	0.3308	-51.4430	-8.82
	0.1194	0.82980	1.84570	1382.4	-1.5596	-69.5867	-55.00
	0.1882	0.86030	1.77360	1384.3	-2.3060	-69.5019	-42.84
	0.2649	0.88180	1.62190	1465.6	-1.8223	-76.5394	-82.98
	0.3510	0.92510	1.53850	1482.4	-3.6523	-75.7502	-77.99
	0.4480	0.96030	1.51400	1531.7	-4.3380	-67.9153	-82.35
	0.5578	0.96460	1.48500	1617.1	-1.3043	-59.1732	-83.31
	0.6836	0.97870	1.40730	1634.7	0.9657	-53.6046	-47.63
	0.8294	1.05980	1.35180	1683.7	-4.3934	-43.6954	-43.75
	1.0000	1.06030	1.60760	1719.2	0.0000	0.0000	0.00

Table.2. Values of densities, viscosities, ultrasonic velocity, Excess molar volumes and Deviation in viscosity and deviation in isentropic compressibility for binary system of n-butyl alcohol and O-nitrotolune at 298.15 and 308.15 K.

Temp K	X_1	ρ (gm /cm^3)	η10^3 (Nsm^{-2})	U (M S^{-1})	V^Ex10^6 (m^3/mole)	Δηx10^3 (Kgm^{-1}s^{-1})	Δksx10^{11} (m^{2}N^{-1})
298.15	0.0000	0.80540	2.52940	1499.6	0.0000	0.0000	0.00
	0.0569	0.83310	2.35250	1515.8	-0.8195	-14.3019	-6.34
	0.1193	0.85980	2.11890	1548.9	-1.4049	-33.9185	-9.52
	0.1880	0.89320	2.00670	1531.8	-2.5991	-41.0172	-10.48
	0.2651	0.92540	1.93240	1566.9	-3.4923	-43.8220	-11.19
	0.3511	0.95760	1.87980	1599.5	-4.2497	-43.9229	-14.38
	0.4480	1.05690	1.82200	1662.4	-11.4269	-43.8898	-49.80
	0.5578	1.07230	1.73500	1682.9	-10.3425	-46.0029	-30.72
	0.6838	1.11090	1.78750	1682.7	-11.2998	-33.1942	-7.89
	0.8296	1.14890	1.83100	1715.1	-12.0733	-20.0976	6.53
	1.0000	1.06920	1.92950	1932.0	0.0000	0.0000	0.00
308.15	0.0000	0.79800	1.99670	1401.4	0.0000	0.0000	0.00
	0.0569	0.82500	1.84770	1441.1	-0.7698	-12.7060	-31.44
	0.1193	0.85150	1.70580	1467.2	-1.3594	-24.4681	-45.34
	0.1880	0.88360	1.60400	1516.5	-2.4488	-31.9749	-73.40
	0.2651	0.91660	1.55200	1517.4	-3.4626	-34.1750	-64.69
	0.3511	0.94880	1.53910	1532.5	-4.2493	-32.1187	-61.27

	0.4480	1.04710	1.49980	1566.6	-11.4740	-32.2783	-90.87
	0.5578	1.06250	1.40870	1598.2	-10.3805	-37.1160	-79.71
	0.6838	1.10080	1.47670	1603.4	-11.3379	-25.4134	-60.98
	0.8296	1.13800	1.51100	1633.3	-12.0581	-16.3103	-48.90
	1.0000	1.06030	1.60760	1665.8	0.0000	0.0000	0.00

Table.3. Values of densities,viscosities, ultrasonic velocity, Excess molar volumes and Deviation in viscosity and deviation in isentropic compressibility for binary system of iso-pentyl alcohol and O-nitrotolune at 298.15 and 308.15 K.

Temp K	X_1	ρ (gm /cm^3)	η 10^3 (Nsm^{-2})	U (M S^{-1})	V^Ex10^6 (m^3/mole)	Δ ηx10^3(Kg m^{-1}s^{-1})	Δksx10^{11} (m^{2}N^{-1})
298.15	0.0000	0.80660	3.74590	1488.6	0.0000	0.0000	0.00
	0.0668	0.83550	3.36850	1499.7	-1.1321	-25.6440	-3.44
	0.1383	0.86450	2.82450	1525.5	-2.1086	-67.0567	-13.52
	0.2163	0.88920	2.60070	1545.6	-2.3422	-75.2688	-13.18
	0.3002	0.95330	1.95640	1601.2	-7.0904	-78.4592	-46.97
	0.3914	0.96100	2.32250	1610.0	-5.0368	-71.2836	-25.24
	0.4910	0.99590	2.13420	1630.7	-5.9413	-72.0223	-17.94
	0.5998	1.08460	2.08160	1642.0	-12.3053	-57.5198	-20.64
	0.7203	1.10090	1.96870	1687.8	-10.8342	-46.9222	-8.59
	0.8528	1.11900	1.92200	1694.5	-9.3612	-27.5249	20.98
	1.0000	1.06920	1.92950	1932.0	0.0000	0.0000	0.00
308.15	0.0000	0.79940	2.79410	1449.2	0.0000	0.0000	0.00
	0.0668	0.82790	2.59620	1450.2	-1.1181	-11.8922	0.08
	0.1383	0.85640	2.16230	1516.7	-2.0672	-46.7987	-44.29
	0.2163	0.88090	2.03580	1538.3	-2.3002	-50.1940	-48.36
	0.3002	0.94430	1.49470	1597.0	-7.0742	-94.3493	-87.92
	0.3914	0.95230	1.79070	1600.2	-5.0371	-53.9284	-66.73
	0.4910	0.98660	1.64660	1619.2	-5.9090	-56.5208	-62.31
	0.5998	1.07570	1.70020	1633.0	-12.4484	-38.2517	-70.82
	0.7203	1.09120	1.67040	1667.9	-10.8883	-26.9344	-58.54
	0.8528	1.10940	1.61370	1678.3	-9.4195	-16.8833	-34.62
	1.0000	1.06030	1.60760	1719.2	0.0000	0.0000	0.00

Table.4. Values of Excess free length (L_f^E), Internal pressure (π^E) ,available volume (V_a^E) and Gibbs free energy(G^{*E}) for binary system of t-butyl alcohol and O-nitrotolune at 298.15 and 308.15 K.

Temp. K	X_1	L_f^E x 10^{-10} m	V_a^Ex10^{-6} m^{3}mol^{-1}	π^E x 10^6 Nm^{-1}	G^{*E} Jmol^{-1}
298.15	0.0	0	0	0	0
	0.0570	0.001	1.927	-15959.1	-739.8
	0.1194	-0.024	1.302	-22943.4	-1111.3
	0.1882	-0.022	2.044	-22947.8	-1127.2
	0.2649	-0.015	4.657	-24995.6	-1274.9
	0.3510	-0.007	5.443	-22176.9	-1300.2
	0.4480	-0.019	6.783	-21590.3	-1217.1

	0.5578	-0.016	6.026	-22318.9	-1328.9
	0.6836	-0.004	7.584	-18106.4	-1144.4
	0.8294	0.009	9.730	-11905.6	-983.2
	1.0	0	0	0	0
308.15	0.0	0	0	0	0
	0.0570	-0.004	0.628	-10031.4	-533.3
	0.1194	-0.024	-0.699	-14073.3	-817.6
	0.1882	-0.020	1.245	-14178.6	-842.9
	0.2649	-0.039	-1.513	-17161.8	-954.3
	0.3510	-0.038	-0.200	-16398.0	-1017.8
	0.4480	-0.042	-0.685	-15036.0	-945.2
	0.5578	-0.044	-3.488	-14437.4	-780.0
	0.6836	-0.027	-1.487	-12346.1	-708.4
	0.8294	-0.025	-1.201	-7710.4	-744.3
	1.0	0	0	0	0

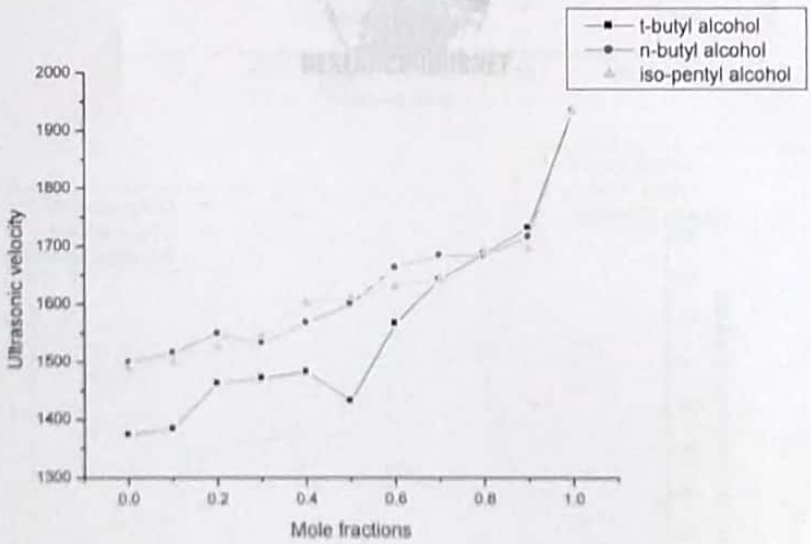
Table.5. Values of Excess free length (L_f^E), Internal pressure (π^E) ,available volume (V_a^E) and Gibbs free energy(G^{*E}) for binary system of n-butyl alcohol and O-nitrotolune at 298.15 and 308.15 K.

Temp. K	X_1	L_f^E x 10^{-10} m	V_a^Ex10^{-6} m^3mol^{-1}	π^E x 10^6 Nm^{-1}	G^{*E} $Jmol^{-1}$
298.15	0.0	0	0	0	0
	0.0569	-0.004	0.977	-3036.9	-156.3
	0.1193	-0.011	1.118	-7074.8	-380.9
	0.1880	-0.004	4.416	-7717.9	-492.6
	0.2651	-0.010	4.840	-8621.1	-549.4
	0.3511	-0.012	5.627	-8789.3	-572.0
	0.4480	-0.031	4.955	-6895.1	-756.3
	0.5578	-0.021	7.008	-7003.6	-767.9
	0.6838	-0.008	10.915	-3755.8	-626.9
	0.8296	0.001	13.176	-429.4	-485.7
	1.0	0	0	0	0
308.15	0.0	0	0	0	0
	0.0569	-0.014	-1.222	-3746.6	-180.7
	0.1193	-0.022	-1.566	-6786.0	-358.3
	0.1880	-0.036	-3.290	-9023.3	-498.6
	0.2651	-0.034	-1.953	-9226.4	-558.8
	0.3511	-0.034	-1.337	-8805.3	-545.3
	0.4480	-0.050	-1.946	-6729.4	-735.0
	0.5578	-0.045	-2.021	-7609.6	-797.5
	0.6838	-0.036	-0.239	-4549.2	-624.6
	0.8296	-0.029	0.133	-1789.2	-500.2
	1.0	0	0	0	0

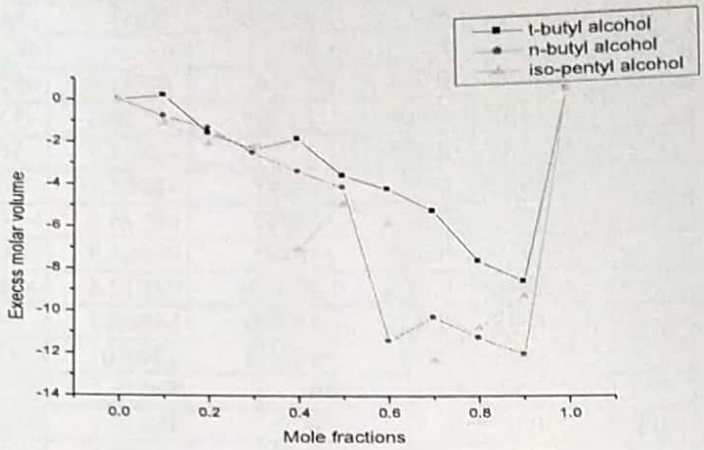
Table.6. Values of Excess free length (L_f^E), Internal pressure (π^E) ,available volume (V_a^E) and Gibbs free energy(G^{*E}) for binary system of iso-pentyl alcohol and O-nitrotolune at 298.15 and 308.15 K.

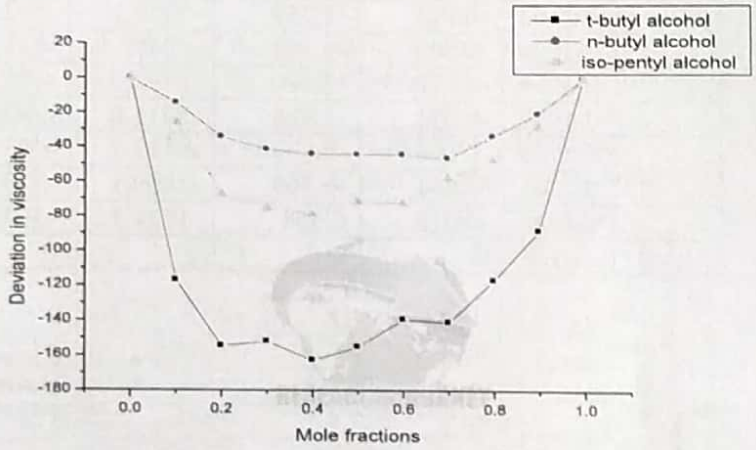
Temp.	X_1	L_f^Ex10^{-10}	V_a^Ex10^{-6}	π^E x 10^6	G^{*E}

K		m	m^3mol^{-1}	Nm^{-1}	$Jmol^{-1}$
298.15	0.0	0	0	0	0
	0.0668	-0.001	1.536	-2751.6	-178.1
	0.1383	-0.006	2.236	-7530.4	-516.9
	0.2163	-0.005	3.567	-8801.9	-596.3
	0.3002	-0.021	2.582	-13887.0	-626.7
	0.3914	-0.011	5.085	-8235.0	-644.3
	0.4910	-0.008	7.030	-7903.9	-707.8
	0.5998	-0.009	10.070	-4072.6	-730.4
	0.7203	-0.003	10.885	-3082.3	-633.8
	0.8528	0.013	14.714	-249.0	-441.4
	1.0	0	0	0	0
308.15	0.0	0	0	0	0
	0.0668	0.000	1.283	-1454.8	-118.5
	0.1383	-0.020	-1.853	-7098.5	-505.4
	0.2163	-0.022	-1.739	-7952.1	-552.5
	0.3002	-0.042	-4.178	-13479.8	-633.1
	0.3914	-0.032	-2.570	-8392.9	-691.0
	0.4910	-0.031	-1.926	-8411.6	-782.3
	0.5998	-0.036	-0.635	-4112.7	-693.3
	0.7203	-0.031	-0.769	-2869.1	-528.3
	0.8528	-0.019	0.954	-1121.1	-394.3
	1.0	0	0	0	0



(a)





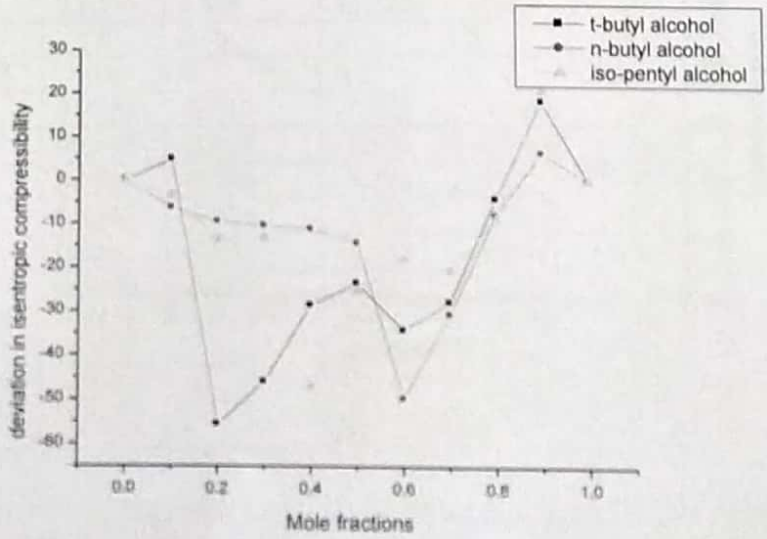
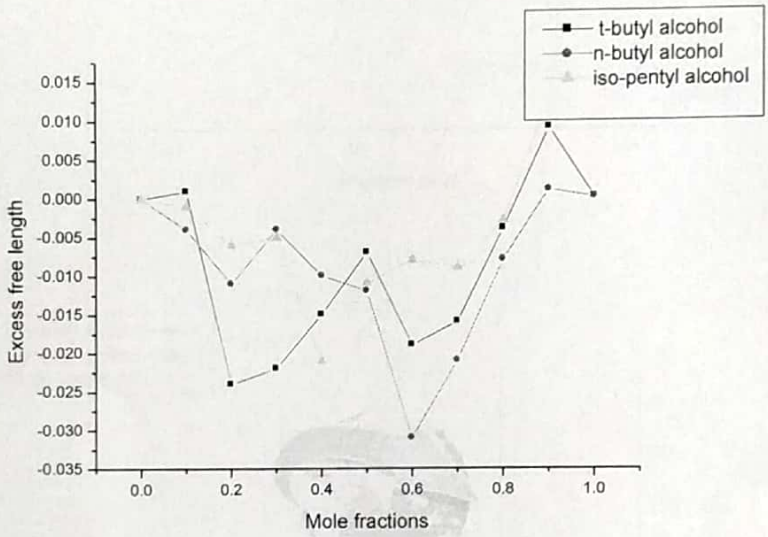
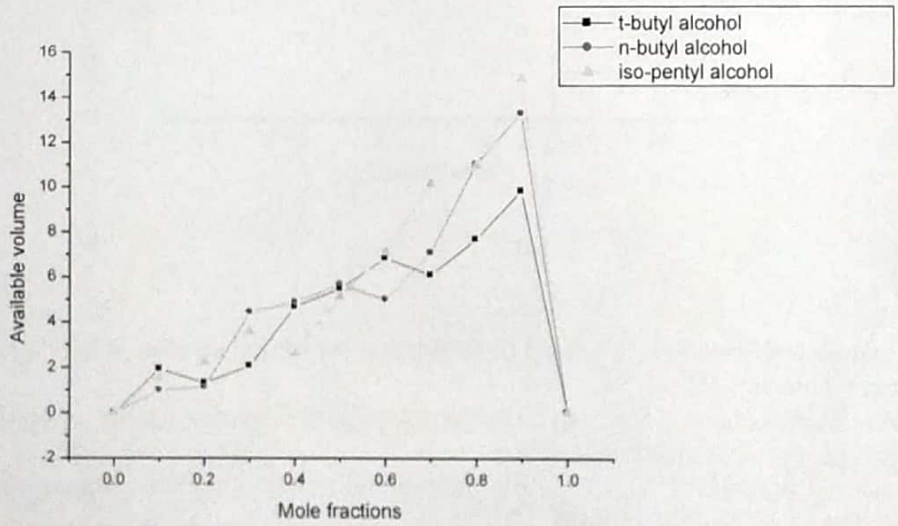


Figure 1.

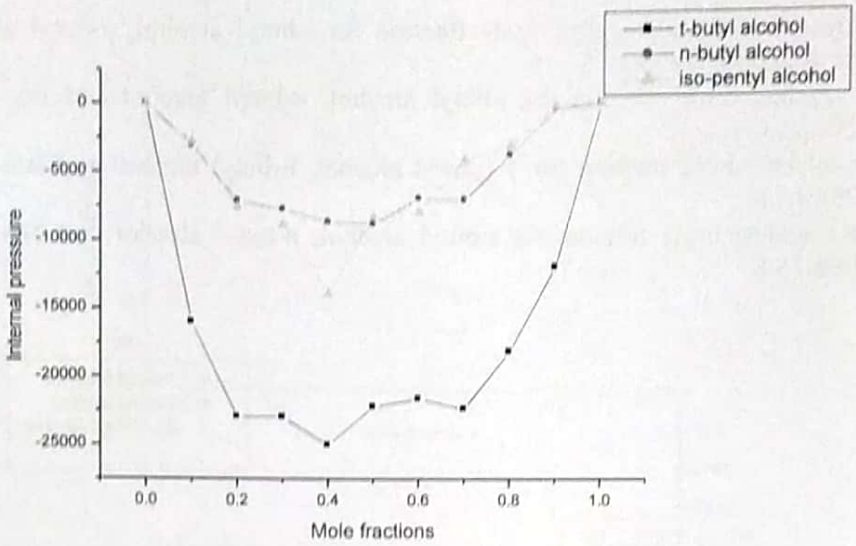
a) Ultrasonic velocity against mole fraction for t-butyl alcohol, n-butyl alcohol and iso-pentyl alcohol at298.15 K
b) V^E against mole fraction for t-butyl alcohol, n-butyl alcohol and iso- pentyl alcohol at298.15 K
c) Δn against mole fraction for 1 t-butyl alcohol, n-butyl alcohol and iso- pentyl alcohol at298.15 K
d) ΔKs against mole fraction for t-butyl alcohol, n-butyl alcohol and iso- pentyl alcohol at298.15 K



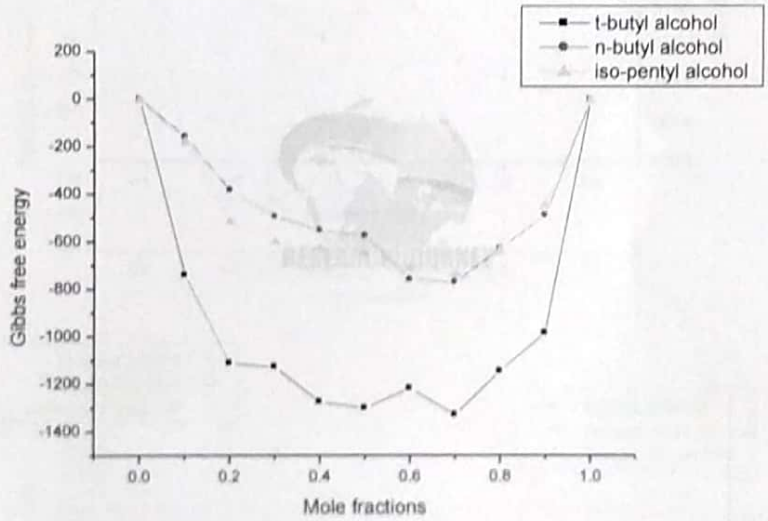
(a)



(b)



(c)



(d)

Figure 2.

a) Excess free length (L_f^E) against mole fraction for t-butyl alcohol ,n-butyl alcohol and iso-pentyl alcohol at298.15 K
b) Available volume (V_a^E) against mole fraction for t-butyl alcohol ,n-butyl alcohol and iso- pentyl alcohol at298.15 K
c) Internal pressure (π^E)against mole fraction for 1 t-butyl alcohol ,n-butyl alcohol and iso-pentyl alcohol at298.15 K
d) Gibbs free energy (G^{*E})against mole fraction for t-butyl alcohol ,n-butyl alcohol and iso-pentyl alcohol at298.15 K