

PHYSICO-CHEMICAL BEHAVIOUR OF BINARY LIQUID MIXTURES OF SOME MONOHYDROXY ALCOHOLS WITH DMSO AS COMMON SOLVENT

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ABSTRACT

Ultrasonic velocity (U), density (ρ) and viscosity (η) measurements have been carried out in three binary liquid mixtures for 1-propanol, 1-butanol and 1-pentanol with dimethyl sulphoxide (DMSO) at 303, 308, 313 K. The experimental data have been used to calculate adiabatic compressibility, free length, free volume, internal pressure, available volume and Gibb's free energy. The excess values of the above parameters have been evaluated and discussed in the light of molecular interaction in the mixtures.

Keywords: *ultrasonic velocity, frelength, Gibb's free energy.*

INTRODUCTION

The ultrasonic velocity measurements find wide applications in characterising the physico-chemical behaviour of liquid mixtures¹⁻³ and in the study of molecular interactions. Ultrasonic velocity of a liquid is related to the binding forces between the atoms or the molecules. Ultrasonic velocity has been adequately employed in understanding the nature of molecular interaction in pure liquids⁴ and binary mixtures. The method of studying the molecular interaction from the knowledge of variation of thermodynamic parameters and their excess values with composition gives an insight into the molecular process⁵⁻⁷. The investigations regarding the molecular association in organic binary mixtures having 1-alkanol group as one of the components is of particular interest, since 1-alkanol group is highly polar and can associate with any other group having some degree of polar attractions. DMSO is aprotic, strongly associated due to highly polar S = 0 group is the molecule and large dipole moment and dielectric constant ($\mu=3.96$ D and $\epsilon = 46.68$ at 298 K)⁸.

The study of DMSO is important because of its utilization in a broad range of applications in medicine⁹. It easily penetrates biological membranes, facilitates chemical transport into biological tissue and it is well known for its cryoprotective effects on biological systems¹⁰⁻¹¹. Also well established is the use of DMSO as an anti-inflammatory agent which commonly has been used for arthritic conditions. DMSO has also been utilized as an in situ free radical scavenger for various cancer treatments. The unique properties of DMSO also give rise to its wide use as a solvent. In view of the importance mentioned, an attempt has been made to elucidate the molecular interactions in the mixtures of dimethyl sulphoxide with 1-propanol, 1-butanol and 1-pentanol respectively at 303, 308 and 313K. Further, the excess values of some of the acoustical and thermodynamical parameters have been calculated from the measurements of ultrasonic velocity, density and viscosity of the mixtures. The excess functions are used to explain intermolecular interactions in these binary mixtures.

EXPERIMENTAL

All the chemicals used in the present research work are analytical reagent (AR) and spectroscopic reagent (SR) grades of minimum assay of 99.9% obtained from E-Merck, Germany and SdFine chemicals, India, which are used as such without further purification. The purities of the above chemicals were checked by density determination at 303, 308 and 313K ± 0.1 K which showed an accuracy of $\pm 1 \times 10^{-4}$ gcm⁻³. The binary liquid mixtures of different known compositions were prepared in stopper measuring flasks. The density, viscosity and velocity were measured as a function of composition of the binary liquid mixture of 1-alkanols with DMSO at 303, 308 and 313K. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.01 kg.m⁻³. The weight of the sample was measured using electronic digital balance with an accuracy of ± 0.1 mg (Model: SHIMADZU AX-200). An Ostwald's viscometer (10ml) was used for the viscosity measurement and efflux time was determined using a digital chronometer to within ± 0.01 s. An ultrasonic interferometer having the frequency of 3 MHz (MITTAL ENTERPRISES, New Delhi, Model: F-81) with an overall accuracy of $\pm 0.1\%$ has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature with an accuracy of ± 0.1 K.

Theory and Calculations

Various physical and thermodynamical parameters are calculated from the measured data such as

$$\text{Adiabatic Compressibility } \beta = \frac{1}{U^2 \rho} \quad \dots(1)$$

$$\text{Intermolecular free length } L_f = K\sqrt{\beta} \quad \dots(2)$$

where K is a temperature dependent constant. Its values are 631×10^{-6} , 636×10^{-6} and 642×10^{-6} respectively at 303, 308 and 313K.

$$\text{Free volume } V_f = \left(\frac{M_{\text{eff}} U}{K \eta} \right)^{3/2} \quad \dots(3)$$

where M_{eff} is the effective molecular weight ($M_{\text{eff}} = \sum m_i x_i$, in which m_i and x_i are the molecular weight and the molefraction of the individual constituents respectively). K is a temperature independent constant which is equal to 4.28×10^9 for all liquids.

$$\text{Internal Pressure } \pi_i = bRT \left(\frac{K\eta}{U} \right)^{1/2} \left(\frac{\rho^{2/3}}{M_{\text{eff}}^{7/6}} \right) \quad \dots(4)$$

where b is the cubic packing which is assumed to be 2 for all liquids and solutions, η is the viscosity, R is a gas constant and T absolute temperature.

$$\text{Available volume } V_a = V_T \left(1 - \frac{U}{U_\infty} \right) \quad \dots(5)$$

where U_∞ is the limiting velocity and is taken as $1600 \text{ m}\cdot\text{s}^{-1}$ and v_T is the molar volume at TK.

The Gibb's free energy can be estimated from the following relation.

$$\Delta G = KT \ln \left(\frac{KT\tau}{h} \right) \quad \dots(6)$$

Where K is the Boltzmann's constant ($1.23 \times 10^{-23} \text{ JK}^{-1}$), T the absolute temperature, ' h ' the Planck's constant and τ is the relaxation time ($\tau = \frac{4}{3} \eta \beta$).

Excess values of the above parameters can be determined using

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

where $A_{\text{id}} = \sum A_i X_i$, A_i is any acoustical parameters and X_i the molefraction of the liquid component.

RESULTS AND DISCUSSION

The experimental values of density, viscosity and ultrasonic velocity, for the three binary liquid systems at 303, 308 and 313K, are given in Table 1. The excess values of acoustical and thermodynamical parameters are presented in Tables 2-3. The variation of excess parameter with the mole fraction of 1-alkanols (x_2) at 303, 308, 313 K are plotted in Figures 1-7, and the curves are drawn using least square fitting.

Table-1: Values of density (ρ) viscosity (η) and ultrasonic velocity (U) for

Molefraction (X_2)	$\rho / (\text{kg m}^{-3})$			$\eta / (\times 10^{-3} \text{ Nsm}^{-2})$			$U / (\text{m.s}^{-1})$		
	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
System-I: DMSO (x_1)+1-propanol (x_2)									
0.0	1085.6	1084.7	1082.6	1.7111	1.5783	1.4294	1441.8	1434.8	1434.2
0.1	1017.0	1015.0	1010.6	1.5069	1.4721	1.3332	1387.7	1377.2	1363.6
0.3	949.1	947.1	945.3	1.4875	1.3939	1.2733	1357.5	1356.2	1355.6
0.5	914.8	907.0	898.3	1.4825	1.3932	1.2538	1341.2	1338.0	1306.0
0.7	863.7	858.8	853.9	1.4644	1.3587	1.2325	1258.5	1231.6	1229.6
0.9	817.4	816.5	812.9	1.4234	1.2589	1.2248	1227.9	1226.1	1223.2
1.0	802.1	801.7	800.3	1.4116	1.2462	1.2013	1216.6	1209.3	1201.1
System-II: DMSO (x_1)+1-butanol (x_2)									
0.0	1085.6	1084.7	1082.6	1.7111	1.5783	1.4294	1441.8	1434.8	1434.2
0.1	1039.2	1036.6	1035.3	1.6434	1.5128	1.3791	1390.0	1377.2	1373.6
0.3	976.7	975.0	971.4	1.6264	1.4991	1.3557	1354.2	1321.0	1310.4
0.5	928.0	923.1	917.7	1.6066	1.4647	1.3371	1306.4	1295.0	1288.9
0.7	864.8	862.3	860.6	1.5863	1.3589	1.2467	1274.1	1264.0	1245.4
0.9	827.2	823.1	816.8	1.5796	1.3424	1.2362	1234.2	1228.6	1223.4
1.0	804.2	803.3	802.2	1.5625	1.3190	1.2019	1220.6	1212.0	1188.8
System-III: DMSO (x_1)+1-pentanol (x_2)									
0.0	1085.6	1084.7	1082.6	1.7111	1.5783	1.4294	1441.8	1434.8	1434.2
0.1	1079.9	1076.0	1074.5	1.7048	1.5822	1.4317	1426.5	1408.8	1392.9
0.3	1061.0	1057.6	1052.0	1.6900	1.5765	1.4286	1360.0	1356.4	1355.4
0.5	1007.8	1003.7	996.0	1.6503	1.5277	1.4140	1340.5	1336.8	1326.8
0.7	886.8	824.2	822.6	1.6250	1.5260	1.4020	1286.7	1286.2	1284.7
0.9	826.9	820.2	802.0	1.6011	1.5213	1.3980	1252.2	1249.2	1245.4
1.0	809.2	807.2	803.2	1.5793	1.5007	1.3925	1240.6	1218.6	1215.9

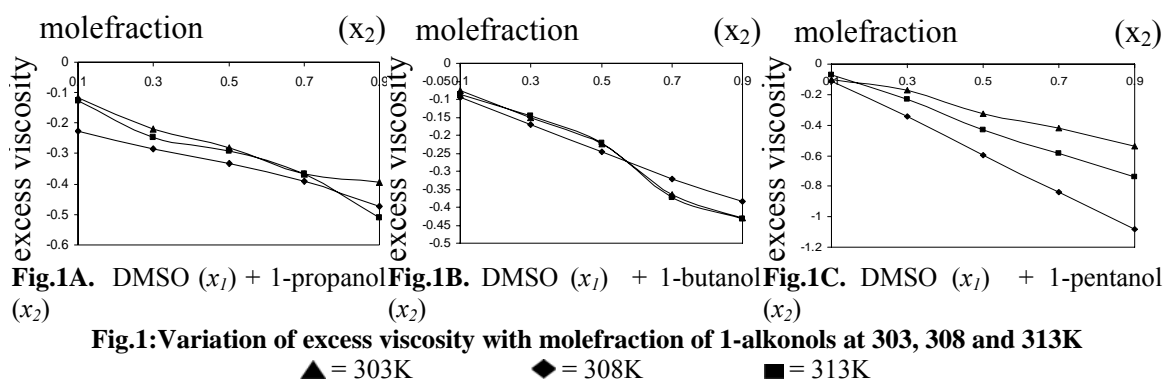
Table-2: Excess values of viscosity (η^E), adiabatic compressibility (β^E) and free length (L_f^E) for

Molefraction (X_2)	$\eta^E / (\times 10^{-3} \text{ Nsm}^{-1})$			$\beta^E / (\times 10^{-10} \text{ m}^2 \text{ N}^{-1})$			$L_f^E / (\times 10^{-10} \text{ m})$		
	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
System-I: DMSO (x_1)+1-propanol (x_2)									
0.1	-0.2247	-0.1274	-0.1174	0.2780	0.3096	0.4138	0.040	0.054	0.069
0.3	-0.2851	-0.2482	-0.2197	0.0951	0.0470	0.0147	0.060	0.028	0.024
0.5	-0.3310	-0.2915	-0.2816	0.3400	0.3453	0.0574	0.070	0.031	0.012
0.7	-0.3901	-0.3684	-0.3652	0.0993	0.3625	0.3352	0.030	0.054	0.056
0.9	-0.4721	-0.5108	-0.3953	0.1090	0.0225	0.0292	0.020	0.012	0.013
System-II: DMSO (x_1)+1-butanol (x_2)									
0.1	-0.0958	-0.0873	-0.0765	0.1634	0.2069	0.2167	0.031	0.053	0.013
0.3	-0.1691	-0.1446	-0.1520	0.0058	0.2132	0.2686	0.023	0.058	0.054
0.5	-0.2452	-0.2226	-0.2231	0.0469	0.0043	0.0092	0.020	0.031	0.028
0.7	-0.3218	-0.3719	-0.3658	0.0095	0.0123	0.1171	0.021	0.026	0.029
0.9	-0.3847	-0.4320	-0.4285	0.0317	0.0116	0.0180	0.009	0.015	0.002
System-III: DMSO (x_1)+1-pentanol (x_2)									
0.1	-0.1141	-0.0719	-0.0980	-0.2383	-0.1684	-0.0732	-0.020	-0.003	-0.002
0.3	-0.3446	-0.2292	-0.1697	-0.4140	-0.4574	-0.4555	-0.034	-0.036	-0.043
0.5	-0.5999	-0.4296	-0.3270	-0.8976	-0.0767	-0.0684	-0.068	-0.073	-0.067
0.7	-0.8408	-0.5823	-0.4216	-0.5572	-0.0246	-0.0219	-0.004	-0.049	-0.046
0.9	-1.0803	-0.7391	-0.5381	-0.0443	-0.0205	-0.1341	-0.018	-0.006	-0.028

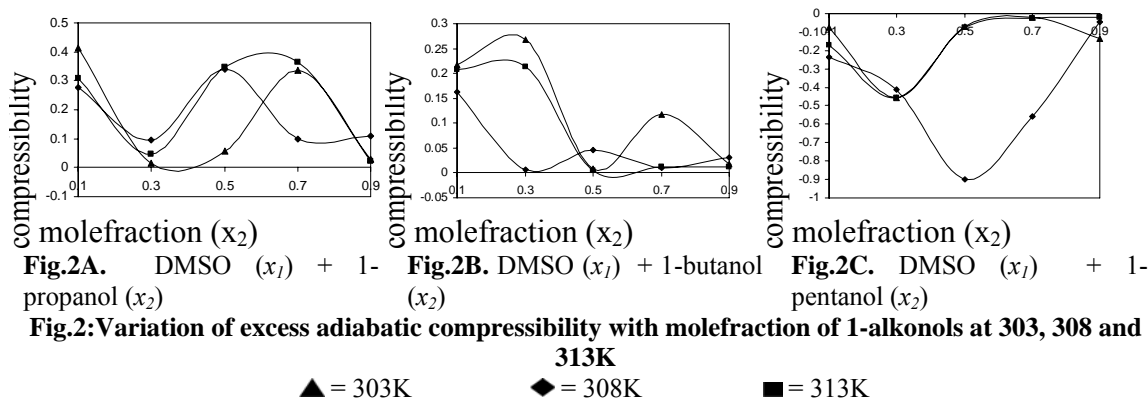
Table-3: Excess values of free volume (V_f^E), internal pressure (π_i^E), available volume (V_a^E) and Gibb's free energy (ΔG^E) for

Molefraction (X_2)	$V_f^E / (\times 10^{-8} \text{ m}^3 \text{ mol}^{-1})$			$\pi_i^E / (\times 10^6 \text{ Nm}^{-2})$			$V_a^E / (\times 10^{-6} \text{ m}^3 \text{ mol}^{-1})$			$\Delta G^E / (\times 10^{-20} \text{ KJmol}^{-1})$		
	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
System-I: DMSO (x_1)+1-propanol (x_2)												
0.1	0.95	0.49	0.74	-60.7	-41.4	-37.9	1.76	1.95	2.56	-0.012	-0.009	-0.007
0.3	1.11	1.16	1.26	-95.1	-87.2	-87.7	1.25	1.00	0.90	-0.041	-0.040	-0.040
0.5	1.53	1.30	1.43	-86.0	-99.0	-105.5	0.31	0.39	1.00	-0.077	-0.072	-0.079
0.7	1.07	1.13	1.57	-111.9	-97.8	-116.3	1.49	2.52	2.41	-0.060	-0.065	-0.068
0.9	1.81	1.62	1.40	-123.2	-106.3	-101.4	0.74	0.50	0.34	-0.001	-0.010	-0.079
System-II: DMSO (x_1)+1-butanol (x_2)												
0.1	0.25	0.30	0.21	-12.1	-13.3	-12.6	1.11	1.39	1.39	-0.001	-0.003	-0.005
0.3	0.54	0.42	0.48	-24.3	-15.5	-18.8	0.21	1.47	1.59	-0.013	-0.011	-0.003
0.5	0.76	0.90	1.06	-25.5	-24.5	-32.0	0.02	0.21	0.13	-0.036	-0.037	-0.035
0.7	1.09	1.84	2.06	-38.7	-70.8	-79.3	0.51	0.39	0.37	-0.055	-0.081	-0.072
0.9	1.72	1.92	2.13	-56.5	-81.3	-94.4	0.83	1.61	0.26	-0.051	-0.073	-0.070
System-III: DMSO (x_1)+1-pentanol (x_2)												
0.1	0.40	0.43	1.24	-88.0	-22.0	-3.1	-0.90	-0.53	-0.17	-0.031	-0.024	-0.009
0.3	0.93	0.85	0.81	-22.4	-10.4	-5.7	-0.86	-1.33	-13.14	-0.073	-0.593	-0.055
0.5	1.91	2.68	1.90	-66.0	-51.0	-39.5	-2.41	-3.11	-2.68	-0.132	-0.115	-1.025
0.7	0.95	1.60	2.32	-79.3	-67.6	-58.3	-0.46	-0.12	-0.33	-	-	-
0.9	1.20	1.67	1.94	-87.15	-83.1	-69.1	-1.73	-1.86	-1.89	0.066	0.079	0.072

The measurement of viscosity in binary mixture yields some reliable information in the study of molecular interaction. Table 1 shows that the values of viscosity decreases with increase in concentration of 1-alkanols. The thermodynamic excess properties are found to be more sensitive towards intermolecular interaction between component molecules of liquid mixtures. The sign and the extent of deviation of these properties from ideality depend on the strength of interaction between unlike molecules¹². According to Fort *et. al.*³ the excess viscosity gives the strength of the molecular interaction between the interacting molecules. For systems where dispersion, induction and dipolar forces which are operated by the values of excess viscosity are found to be negative, whereas the existence of specific interactions leading to the formation of complexes in liquid mixtures tend to make excess viscosity positive. The excess viscosity (Fig. 1) is negative through the whole range of concentration in all the three systems. From the analysis and close observation, it is found that they decrease with increase in concentration of 1-alkanols, but however it found to increase with elevation of temperature. The large negative values of excess viscosity for all the systems can be attributed to the presence of the dispersion, induction, and dipolar forces between the components.



Further, the Fig.2 shows that the excess values of adiabatic compressibilities are positive and non-linear variation are observed in systems I and II, but however it is found to be negative in system III. Fort *et. al.*³ found that the negative value of excess compressibilities indicates greater interaction between the components of the mixtures. Positive values in excess properties correspond mainly to the existence of dispersive forces. Dispersive forces which are generally present in systems I & II would make positive contribution.



The negative value of β^E is associated with a structure forming tendency while a positive value is taken to indicate a structure breaking tendency due to hetero-molecular interaction between the

component molecules of the mixtures. The negative β^E values for binary mixtures indicate, the formation of H-bonds (between the $-O=S-$ group of $(CH_3)_2SO$ and the $-OH$ group 1-alkanol). The positive excess adiabatic compressibility which indicates loosely packed molecules in the mixtures results due to shape and size. In the present investigation the positive deviations of β^E in systems I & II have been attributed to dispersive forces that show weak molecular interaction between the unlike molecules.

The Fig.3 shows that the non-linear variation of excess free length is positive in systems I and II whereas negative in system III. According to Ramamoorthy *et. al.*¹³ negative values of excess intermolecular free length L_f^E indicate that sound waves cover longer distances due to decrease in intermolecular free length ascribing the dominant nature of hydrogen bond interaction between unlike molecules. Fort *et. al.*³ indicated that the positive values of excess free length should be attributed to the dispersive forces, and negative excess values should be due to charge transfer and hydrogen bond formation. In the present study the positive contribution of L_f^E in systems I and II shows a weak interaction while, negative contribution in system III prevails the existence of greater interactions. Spencer *et. al.*¹⁴ have also reported a similar observation on the basis of excess values of free length.

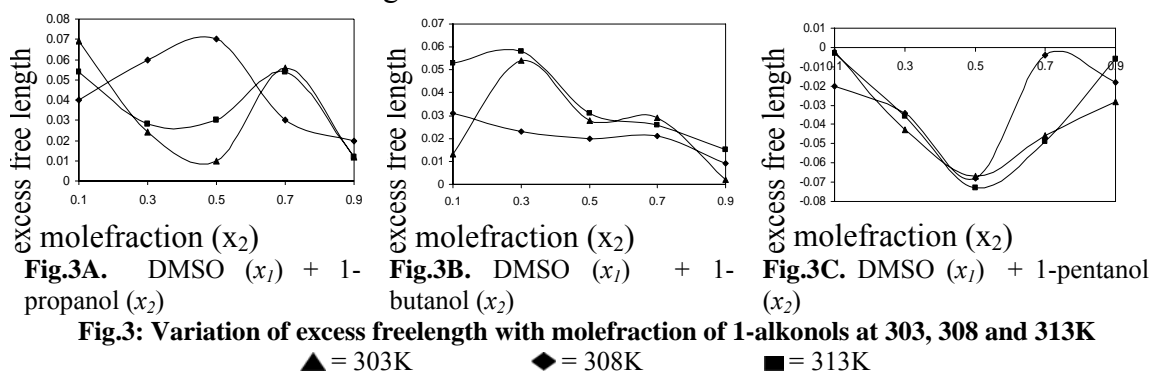
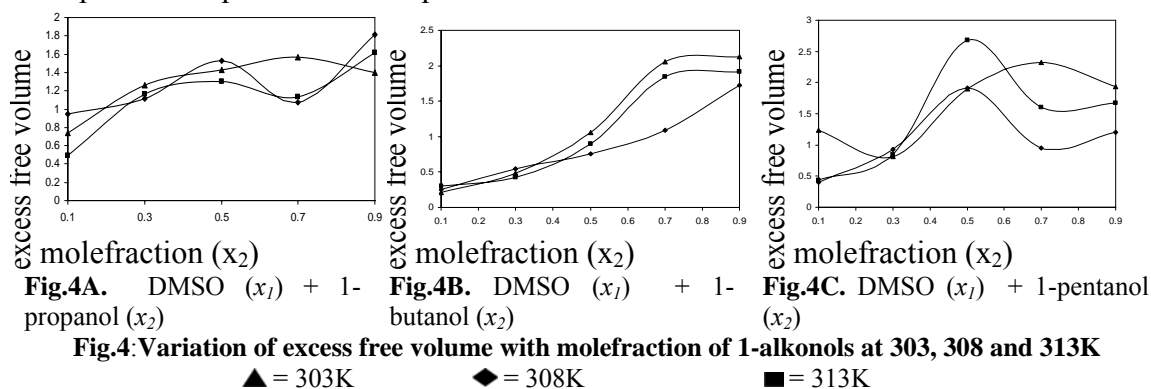
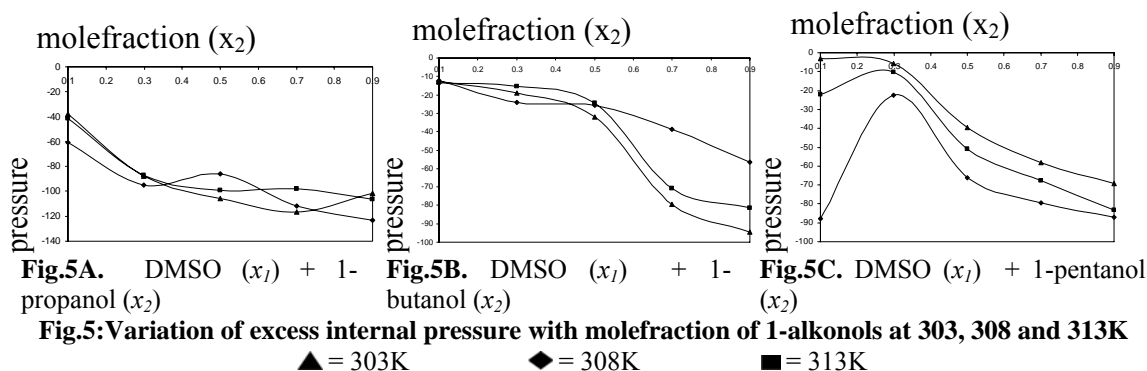


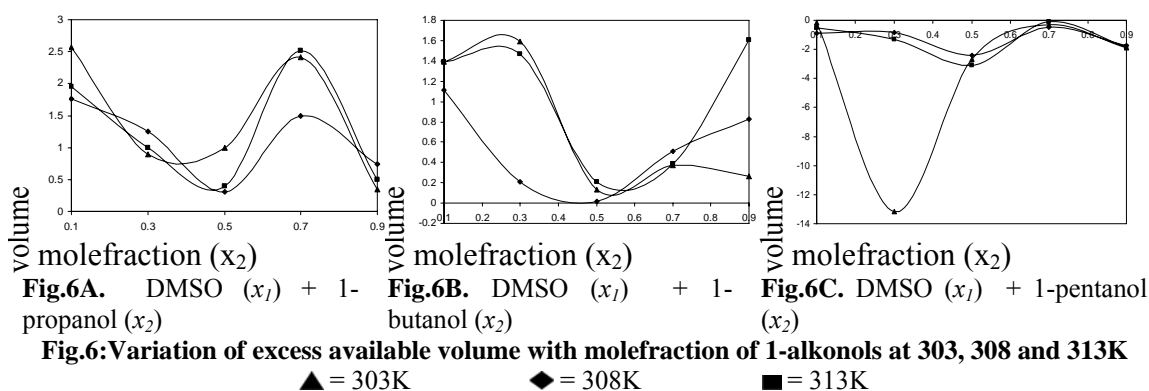
Fig.4 gives a qualitative picture of the excess free volume for the binary liquid mixtures. The values of V_f^E are found to be positive and vary non-linear in all the three systems studied. For some binary liquid mixture, Fort *et. al.*³ notice the negative excess free volume tends to decrease as the strength of the interaction between the unlike molecules increases although they do not parallel with the excess compressibilities. However, in the present investigation a trend observed is exceptional and non-linear which may be due to the disruption of molecular associations of dipole-dipole and dipole-induced dipole interactions.



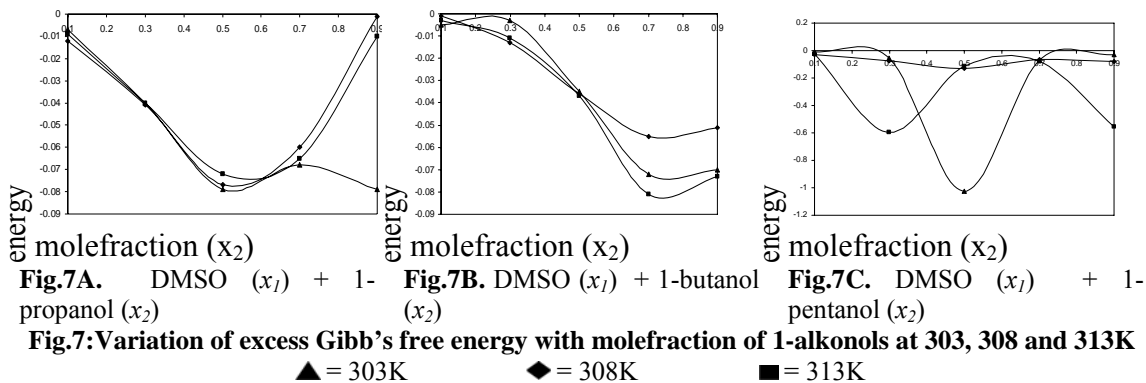
The excess internal pressures (Fig.5) are negative but it is found to be decreasing with increasing concentration of 1-alkanols in all the three system studied. The negative values of π_1^E indicate that only dispersion and dipolar forces are operating with complete absence of specific interaction.



The excess available volume (Fig.6) is positive and varies non-linearly in system I and II but negative in system III. It is observed from the study of Fort *et. al.*³ when interaction occurs between the molecules of the two species the excess available volume becomes increasingly negative. This is due to the closer approach of unlike molecules. The positive excess available volume obtained in systems I and II reflects the absence of stronger interaction. Dissociation also leads to positive contribution. The negative excess available volume obtained in system III shows the presence of specific interactions.



The variation of excess Gibb's free energy (Fig.7) is found to be negative in all the three systems studied. According to Reed *et. al.*¹⁵ the positive deviation in ΔG^E may be attributed to specific interactions, hydrogen bonding and charge transfer, whereas the negative deviations may be ascribed to dispersion forces with systems. In the present investigation it is found that the dipolar and dispersive forces are mainly operating in the behaviour of ΔG^E . Recently Ali *et. al.*¹⁶ attributes the increasing positive values of ΔG^E in few binary liquid mixtures, to hydrogen bond formation between unlike molecules, which supports the present investigation.



CONCLUSION

The excess ultrasonic properties reveal that the existence of molecular interaction in the binary mixtures. The present investigation shows that greater molecular interaction exists in the 1-pentanol mixtures which may be due to hydrogen bond formation and weak molecular interaction that exists in the 1-propanol and 1-butanol mixtures which may be due to the dominance of dispersion forces and dipolar interaction between the unlike molecules. The interaction tends to be weaker with rise in temperature which may due to weak intermolecular forces and thermal dispersion forces. The existence of molecular interaction in the mixture is in the order: 1-pentanol > 1-butanol > 1-propanol.

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