



ISSN: 0976-3031

Available Online at <http://www.recentscientific.com>

International Journal of Recent Scientific Research
Vol. 3, Issue, 7, pp. 627 - 636, July, 2012

International Journal
of Recent Scientific
Research

RESEARCH ARTICLE

THERMO-ACOUSTICAL AND EXCESS THERMODYNAMIC STUDIES OF TERNARY LIQUID MIXTURES OF PRIMARY ALKANOLS IN AQUEOUS MIXED SOLVENT SYSTEMS AT 303.15, 308.15 AND 313.15 K

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ARTICLE INFO

Article History:

Received 11th June, 2012
Received in revised form 20th, June, 2012
Accepted 10th July, 2012
Published online 30th July, 2012

Key words:

adiabatic compressibility, dipole-dipole interaction, hydrogen bonding, internal pressure, intermolecular free length.

ABSTRACT

The observed experimental parameters such as density (ρ), viscosity (η) and ultrasonic velocity (U) of ternary liquid mixtures of primary alkanols such as 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol added in the fixed binary solvent mixtures of (ratio 4:2) N-N dimethyl formamide (DMF) and methyl isobutyl ketone (MIBK) at 303.15, 308.15 and 313.15K were determined. The observed experimental data have been utilized to evaluate some of the excess thermo acoustical parameters such as adiabatic compressibility (β^E), intermolecular free length (L_f^E), free volume (V_f^E), internal pressure (π_i^E), Gibb's energy (ΔG^E), viscosity (η^E) molar volume (V_m^E) and Grunberg's interaction parameter (d). Our present study predicts the interaction between DM and 1-alkanols is due to hydrogen bonding and latter there seems to be a dissociation of associated structure of 1-alkanols. It is also noticed that on further addition of DMF causes such rupturing of hydrogen bonded association of 1-alkanols and leading to subsequent weakening of interaction between MIBK and 1-alkanols as well as between DMF and 1-alkanols. However, our further investigation reveals that the elevation of temperature over the liquid mixtures leading to strengthening of their interactions.

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INTRODUCTION

Measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interaction in pure liquid and liquid mixtures. Ultrasonic studies of aqueous mixed solvent systems are of importance because of their extensive use in textile, leather and pharmaceutical industries. Organic solvents whose miscibility with water is unlimited usually form H-bonds in aqueous solutions. Some solvents also present auto-association by hydrogen bonds in pure state but others do not. The functional group of organic solvent can form H-bonds with water due to hydrophilic effects, while the hydrocarbon part of the organic solvents is responsible for hydrophobic part. The practical application of mixed solvents rather than single solvent in industrial and biological process has been recognized all over the world as they provide a wide choice of solutions with appropriate properties (Ali *et al.*, 2001).

The evaluated excess quantities from experimental acoustical data have been interpreted in terms of the differences in the size of the molecule as well as the strength of specific and non specific interactions between components of the mixture. Further, measurements of excess thermodynamic properties are found to be greatly significant in studying the structural changes associated with the liquids. They also provide important information about molecular packing, molecular motion and various types of intermolecular interactions and their strength influenced by the size, shape and the chemical nature of component molecules (Aminabhari

et al., 1996). This in turn helps in bringing out the facts which can have positive implementation for both industry as well as the building process. A thorough knowledge of thermodynamic and transport properties of ternary liquid systems is essential in many industrial applications such as design, calculations, heat transfer, mass transfer, fluid flow and so forth (Nikam *et al.*, 2003).

The present study deals with the study of excess thermodynamic and transport of some aqueous mixed solvent system at different temperatures. The liquids under investigation have been chosen on the basis of their industrial applications. These applications have greatly stimulated the need for extensive information on the thermodynamic, acoustic and transport properties of these solvents and their mixtures Oswel *et al.*, 2001, Thirumaran and Karthikeyan (2011)

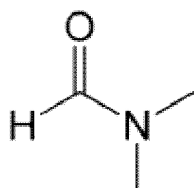
In general, the hydroxyl group makes the alcohol molecule polar. Those groups can form hydrogen bonds to one another and to other compounds. This hydrogen bonding means that alcohols can be used as protic solvents. Two opposing solubility trends in alcohols are: the tendency of the polar OH to promote solubility in water, and the tendency of the carbon chain to resist it. All simple alcohols are miscible in organic solvents. The simple alcohols that are used in present study are 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol. Alkanols are polar liquids, strongly self-associated by hydrogen bonding to the extent of polymerization that may differ depending on temperature, chain length, and position of the OH group. For the alcohols which are highly associated in the

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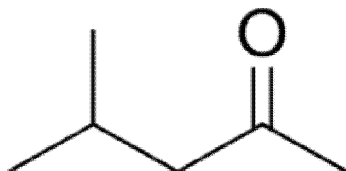
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pure state, breaking of the H-bonds followed by specific interactions occurs upon mixing with highly polar solvents. The alkanol chain length and shifting the position of the hydroxyl group of the alkanols are important parameters that must be taken into account to explain the behavior interaction of the amide + 1- alkanol mixtures. It is well known that amides interact with alkanols by dipole-dipole interactions, and form some hydrogen-bonded complexes or hetero-associates Eberhardt and Raines, 1994; Eaton *et al.*, 1989; Schmid and Brodbek, 1985; Pikkarainen, 1991. On the basis of those studies, it is interesting to note that the thermodynamic results of the addition of the amide group with alkanols to obtain some information on the molecular interactions.

On the other hand, dimethylformamide is an organic compound abbreviated as DMF, this colourless liquid is miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions. Pure dimethylformamide is odorless. Dimethylformamide is a polar (hydrophilic) aprotic solvent with a high boiling point. Dimethylformamide can be synthesized from methyl formate and dimethylamine or by reaction of dimethylamine with carbon monoxide. The primary use of dimethylformamide is as a solvent with low evaporation rate. DMF is used in the production of acrylic fibers and plastics. It is also used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, and in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings. The structure of N, N- dimethylformamide is given as



Methyl isobutyl ketone (MIBK) is an organic compound. This colourless liquid, an aliphatic ketone, is widely used as a solvent. MIBK has quite low solubility in water, making it useful for liquid-liquid extraction. It has a similar polarity to ethyl acetate, but greater stability towards aqueous acid and base. It can be used to extract gold, silver and other precious metals from cyanide solutions, such as those found at gold mines, to determine the levels of those dissolved metals. MIBK is used as a solvent for nitrocellulose, lacquers, and certain polymers and resins. The structure of Methyl isobutyl ketone (MIBK) is given as



Owing to these physical characteristics of N,N-dimethylformamide, methyl isobutyl ketone and primary alkanols, which motivated the authors to carry out the present study of molecular interactions of ternary liquids mixtures of primary alkanols with binary solvent mixtures of N,N-dimethylformamide (DMF) and methyl isobutyl ketone (MIBK) in the fixed ratio of 4:2 respectively at different temperatures. As no systematic study was carried out the

combined effect of amide and ketone as binary solvents in which primary alkanols were added as solutes at varying temperatures, the present investigation was carried out. The present ternary liquid systems taken up by the authors at different temperatures, say at 303.15, 308.15 and 313.15 K are

System I: 1-pentanol + N, N-dimethylformamide (DMF) + Methyl isobutyl ketone (MIBK)

System II: 1-hexanol + N, N-dimethylformamide (DMF) + Methyl isobutyl ketone (MIBK)

System III: 1-heptanol + N, N-dimethylformamide (DMF) + Methyl isobutyl ketone (MIBK)

System IV: 1-octanol + N, N-dimethylformamide (DMF) + Methyl isobutyl ketone (MIBK)

Experimental

In the present work, the chemicals, which have been used are analytical reagent (AR) and spectroscopic reagent (SR) grades of minimum assay of 99.9% obtained from E-Merk, Germany and Sd fine chemicals, India. The purities of the above chemicals were checked by the density measurements at 303.15, 308.15 and 313.15K and were compared with available literature values. Kumari *et al.*, (2009), Radhama *et al.*, (2008), Mozo *et al.*, (2008), Hasan *et al.*, (2006), Hasan *et al.*, (2006), Bhattacharjee and Roy (2010), Nikam *et al.*, (1998), Sharma *et al.*, (2009), Das *et al.*, (2009), Yang *et al.*, (2008), Garcia *et al.*, (2008) The ternary liquid mixtures of different known composition were prepared by mole fraction basis. The density, viscosity and ultrasonic velocity were measured as a function of the ternary liquid mixture of primary alkanols which were added to the fixed binary mixtures of DMF and MIBK at 303.15, 308.15 and 313.15K. For this purpose, binary liquid mixtures of DMF and MIBK with a fixed ratio $X_2/X_3 = 4:2$ respectively were prepared and taken. The density was determined using a specific gravity bottle (5ml) by relative measurement method. The weight of the sample was measured using an electronic digital balance with an accuracy of ± 0.1 mg (Model: Shimadzu, Japan Make, AX-200). An Ostwald's viscometer (10ml) was used for the viscosity measurement. Efflux time was determined by using a digital chronometer to within ± 0.001 s. An Ultrasonic Interferometer having a frequency of 2 MHz (Mittal Enterprises, New Delhi. Model: F-81) has been used for velocity measurement. The overall accuracy in the velocity measurement is $\pm 2\text{ms}^{-1}$. An electronically digital operated constant temperature water bath (RAAGA Industries, Chennai) has been used to circulate water through the double walled measuring cell make up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is ± 0.1 K.

RESULTS AND DISCUSSION

In the present study, we reported the values of density, viscosity and ultrasonic velocity which have been measured for the four ternary liquid mixtures at 303.15, 308.15, and 313.15 K. The Tables 1 and 2 provide the experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (U) of pure liquids and for the ternary systems at 303.15, 308.15, and 313.15 K. The excess values of viscosity (η^E), adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E), internal pressure (π_i^E) Gibbs Energy (ΔG^E), excess molar volume (V_m^E) and Grunberg and Nissan's interaction parameter (d) are listed in Table 3-5. Similarly the

Table 1 Values of density (ρ), viscosity (η) and ultrasonic velocity (U) of pure organic liquids

Organic Liquids	Temp. (K)	Density $\rho / (\text{kg.m}^{-3})$			Viscosity $\eta / (\times 10^{-3} \text{ NSm}^{-2})$			Ultrasonic velocity U / (ms^{-1})		
		P.W*	Ref1	Ref2	P.W*	Ref1	Ref2	P.W*	Ref1	Ref2
1-Pentanol	303.15	809.68	807.36 ⁽³⁾	807.39 ⁽³⁾	2.9422	2.933 ⁽⁴⁾		1257.28	1258.2 ⁽⁵⁾	
	308.15	802.79			2.2968			1243.36		
	313.15	799.65			1.8825			1224.56		
1-Hexanol	303.15	811.02	811.72 ⁽³⁾	811.84 ⁽⁴⁾	3.7730	3.765 ⁽⁴⁾	3.762 ⁽⁴⁾	1284.72	1285.6 ⁽⁵⁾	
	308.15	807.43	808.30 ⁽⁷⁾		3.3789	3.398 ⁽⁷⁾		1266.70		
	313.15	804.58	804.28 ⁽⁹⁾	804.60 ⁽⁹⁾	2.9462	2.934 ⁽⁹⁾	2.966 ⁽⁹⁾	1253.44		
1-Heptanol	303.15	813.73	814.80 ⁽⁴⁾		4.7851	4.771 ⁽⁷⁾		1311.08	1313 ⁽⁴⁾	1313 ⁽⁵⁾
	308.15	811.08	812.60 ⁽⁷⁾		4.2836	4.266 ⁽⁷⁾		1295.76		
	313.15	809.93			3.7560			1276.00		
1-Octanol	303.15	816.48	817.52 ⁽⁵⁾	818.34 ⁽⁵⁾	6.2611	6.298 ⁽⁵⁾	6.125 ⁽⁷⁾	1335.16	1339 ⁽⁵⁾	
	308.15	814.35	814.20 ⁽⁶⁾	813.47 ⁽⁷⁾	5.2680	5.256 ⁽⁶⁾	5.250 ⁽⁷⁾	1317.96		
	313.15	811.53			4.3930			1297.84		
DMF	303.15	938.61	939.50 ⁽¹⁰⁾	938.87 ⁽¹¹⁾	0.7528	0.7560 ⁽¹⁰⁾		1476.60		
	308.15	935.18	935.71 ⁽⁸⁾	935.61 ⁽¹¹⁾	0.7071	0.7063 ⁽⁸⁾		1465.44		
	313.15	929.93	930.73 ⁽⁸⁾	929.54 ⁽¹¹⁾	0.6678	0.6683 ⁽⁸⁾	0.6640 ⁽¹⁰⁾	1453.69		
MIBK	303.15	791.80	791.27 ⁽¹⁾	791.27 ⁽²⁾	0.6477			1168.12	1170 ⁽¹⁾	
	308.15	789.03			0.5996			1151.04		
	313.15	785.66			0.5617			1134.96		

PW: Present work

figure 1 and 2 respectively represents the variation of excess Gibb's free energy and excess molar volume with mole fraction.

The thermodynamic excess properties are found to be more sensitive towards intermolecular interaction between the component molecules of liquid mixtures. The sign and extent of deviation of excess properties depend on the strength of interaction between unlike molecules (Mahan *et al.*, 2002). According to Fort and Moore (1965) the variation of 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, where as the existence of specific interactions leading to the specific formation of complexes in liquid mixtures tends to make excess viscosity positive. In the present study, the values of excess viscosity is positive with the absence of alkanols (x_1) but it exhibits negative with increasing the molar concentration of alkanols in all the four systems. From the analysis and close observation it is found that the excess values of viscosity are increasing with increase in mole fraction of alkanols (x_1) and also with the rising temperature. This behavior shows that the existence of molecular interaction between the components of mixture for all the systems studied.

The perusal of Table 3 shows excess adiabatic compressibility (β^E) values which are found to be negative over the whole composition range for all the liquid mixtures and temperature too. Further these values are increased with the increasing mole fraction of alkanols (x_1) and temperature as well. Fort and Moore (1965) found that the negative value of excess adiabatic compressibility indicated greater interaction between the components of the mixtures. Further the negative value of β^E is associated with structure making tendency while a positive value is taken to indicate the structure breaking tendency Thirumaran and Ramesh (2009) due to hetero-molecular interaction between the component molecules of the mixture. In the present investigation, the negative β^E values for all the four liquid ternary systems may

be attributed to the rupture of hydrogen bond between alkanols and the solvent mixtures. Further it is noticed that the increasing trend of negative value of β^E get strengthened with elevation of temperature in all the systems studied.

DMF is an eminently suitable solvent for salts or compounds with a high molecular weight owing to the combined action of its small molecule, and its ability to form complexes. Electron diffraction (Schultz and Hargittai 1993) and microwave studies (Elzaro 1973) for gaseous DMF reveal that all atoms except the methyl hydrogen lie in one plane analogous results were obtained for the liquid DMF Ohtaki *et al.*, (1983), Jorgensen and Swenson(1985), Chalaris and Samios(2000), Radnai *et al.*, (1988).

The resonance structure of DMF is shown in below:



The negative pole in DMF is on an oxygen atom that juts out from the rest of the molecule and this oxygen atom is the best hydrogen bond acceptor. Through unshared pairs of electrons on these negatively charged, well-exposed atoms are solvated very strongly. The positive pole on the other hand, is buried within the molecule. In DMF, the presence of two electrons repelling $-\text{CH}_3$ groups make the lone pair at nitrogen still more perceptible towards donation. Thus, it may be argued that the DMF is actually the donator of nitrogen electron pairs (Venkatesu 2010).

The interactions between the carbonyl carbon group of ketone and solvents with polar group of amides, such as DMF play a crucial role in the structural effects, molecular level and for practical applications. A comparison of the dipole moments of ketones ($\mu = 4.2\text{D}$) with the corresponding alkanols (for 1-pentanol $\mu = 1.7\text{D}$, 1-hexanol $\mu = 1.8\text{D}$, 1-heptanol $\mu = 1.9\text{D}$ and 1-octanol $\mu = 2\text{D}$) shows that the ketones have higher dipole moments than the corresponding alkanols. Therefore, ketones are also polar and

Table 2 Values of density (ρ), viscosity (η) and ultrasonic velocity (U) of primary alkanols with solvent mixture of DMF and MIBK at 303.15, 308.15 and 313.15 K

Mole fraction (X_1)	ρ (kg.m ⁻³)			η ($\times 10^{-3}$ NSm ⁻²)			U (ms ⁻¹)		
	Temperature (K)								
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
1-Pentanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]									
0.0000	925.5628	922.1843	919.3428	0.7902	0.7368	0.6781	1382.44	1362.76	1343.32
0.1000	860.8134	858.4926	856.1208	0.8350	0.7697	0.7135	1304.02	1293.12	1275.20
0.2999	847.9635	844.9656	842.4145	0.9666	0.8840	0.8103	1296.40	1280.08	1264.48
0.4997	833.9130	830.7610	828.5869	1.1844	1.0704	0.9671	1285.76	1270.48	1252.40
0.7000	821.6004	818.1786	816.1017	1.5493	1.3694	1.2159	1277.68	1257.76	1245.90
0.9004	809.8231	806.3937	804.2877	2.2449	1.9282	1.6777	1264.16	1248.80	1232.40
1-Hexanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]									
0.0000	925.5628	922.1843	919.3428	0.7902	0.7368	0.6781	1382.44	1362.76	1343.32
0.0999	863.8841	859.1623	857.1820	0.8674	0.7925	0.7374	1323.08	1303.91	1284.64
0.2999	849.5715	846.0371	843.6228	1.0407	0.9603	0.8823	1306.81	1296.72	1278.08
0.4998	836.3852	833.1084	830.8581	1.2562	1.1121	0.9988	1299.28	1284.32	1268.33
0.7000	823.5372	820.7618	818.4442	1.8752	1.6292	1.4482	1288.43	1274.05	1255.41
0.9003	810.0389	807.4741	805.8635	2.8826	2.4508	2.1093	1280.79	1261.48	1247.22
1-Heptanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]									
0.0000	925.5628	922.1843	919.3428	0.7902	0.7368	0.6781	1382.44	1362.76	1343.32
0.0999	865.6718	861.2516	859.3195	0.8898	0.8165	0.7601	1357.20	1336.75	1316.27
0.2999	851.4296	848.9982	846.1826	1.0950	0.9983	0.9339	1345.41	1325.62	1306.07
0.4998	839.7810	836.0165	834.3421	1.6324	1.3756	1.1390	1334.03	1315.12	1296.45
0.7000	825.9158	822.7618	819.9176	2.4976	2.2058	1.9203	1324.14	1308.03	1288.14
0.9003	812.0983	809.4741	807.7983	3.5620	3.0879	2.8279	1320.26	1301.15	1275.94
1-Octanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]									
0.0000	925.5628	922.1843	919.3428	0.7902	0.7368	0.6781	1382.44	1362.76	1343.32
0.0999	868.8434	865.0552	862.0150	0.9203	0.8431	0.7454	1377.26	1357.68	1338.06
0.2999	855.1925	853.0015	850.7380	1.2118	1.1098	0.9936	1370.72	1349.59	1328.62
0.4998	843.4152	839.8763	836.9103	2.1849	1.9965	1.8006	1361.18	1341.61	1320.77
0.7000	830.2995	827.0190	824.8279	3.8026	3.5295	3.2326	1353.66	1331.73	1312.58
0.9004	815.3102	810.9474	808.6440	5.3289	4.8660	4.4086	1345.76	1321.68	1305.14

Table 3 Excess values of viscosity (η^E), adiabatic compressibility (β^E) and free length (L_f^E) of primary alkanols with solvent mixture of DMF and MIBK at 303.15, 308.15 and 313.15 K

Mole fraction (X_1)	η^E ($\times 10^{-3}$ NSm ⁻²)			$\beta^E / (\times 10^{-10} \text{m}^2 \text{N}^{-1})$			$L_f^E / \times 10^{-10} \text{m}$		
	Temperature (K)								
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
1-Pentanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]									
0.0000	0.0725	0.0656	0.0457	-0.6889	-0.6685	-0.6576	-0.0157	-0.0301	-0.0308
0.1000	-0.7254	-0.4396	-0.2915	-0.3427	-0.3237	-0.3039	-0.0247	-0.0092	-0.0088
0.2999	-0.6448	-0.4130	-0.2899	-0.2510	-0.2436	-0.2344	-0.0182	-0.0080	-0.0068
0.4997	-0.4757	-0.2746	-0.1969	-0.1834	-0.1774	-0.1763	-0.0136	-0.0058	-0.0055
0.7000	-0.4181	-0.2066	-0.0802	-0.1347	-0.0852	-0.0518	-0.0075	-0.0046	-0.0014
0.9004	-0.1051	-0.0641	-0.0439	-0.0612	-0.0495	-0.0124	-0.0037	-0.0017	-0.0003
1-Hexanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]									
0.0000	0.0725	0.0656	0.0457	-0.6889	-0.6685	-0.6576	-0.0157	-0.0301	-0.0308
0.0999	-0.9885	-0.9373	-0.8037	-0.2614	-0.2174	-0.2122	-0.0175	-0.0068	-0.0066
0.2999	-0.9811	-0.9124	-0.7900	-0.2105	-0.1849	-0.1838	-0.0171	-0.0066	-0.0058
0.4998	-0.5933	-0.6581	-0.6062	-0.2041	-0.1767	-0.1644	-0.0133	-0.0063	-0.0052
0.7000	-0.5857	-0.5229	-0.4440	-0.1892	-0.1681	-0.1590	-0.0109	-0.0057	-0.0049
0.9003	-0.1555	-0.1492	-0.1261	-0.1843	-0.1577	-0.1519	-0.0075	-0.0043	-0.0038
1-Heptanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]									
0.0000	0.0725	0.0656	0.0457	-0.6889	-0.6685	-0.6576	-0.0157	-0.0301	-0.0308
0.0999	-1.1181	-1.1010	-1.0545	-0.1515	-0.1108	-0.0931	-0.0064	-0.0061	-0.0052
0.2999	-1.0672	-0.9940	-0.8985	-0.0955	-0.0583	-0.0551	-0.0051	-0.0041	-0.0038
0.4998	-0.8425	-0.8355	-0.6352	-0.0542	-0.0376	-0.0306	-0.0043	-0.0020	-0.0016
0.7000	-0.8175	-0.7562	-0.6166	-0.0265	-0.0126	-0.0040	-0.0039	-0.0014	-0.0011
0.9003	-0.2342	-0.2156	-0.1843	-0.0088	-0.0030	-0.0004	-0.0012	-0.0004	-0.0003
1-Octanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]									
0.0000	0.0725	0.0656	0.0457	-0.6889	-0.6685	-0.6576	-0.0157	-0.0301	-0.0308
0.0999	-1.3034	-0.9721	-0.7666	-0.3272	-0.2923	-0.2689	-0.0145	-0.0144	-0.0126
0.2999	-1.1683	-0.9400	-0.7113	-0.2768	-0.2393	-0.2151	-0.0115	-0.0114	-0.0109
0.4998	-0.7954	-0.3593	-0.3932	-0.2067	-0.1730	-0.1504	-0.0082	-0.0078	-0.0068
0.7000	-0.3761	-0.2873	-0.2627	-0.1380	-0.0883	-0.0817	-0.0045	-0.0039	-0.0025
0.9004	-0.3512	-0.0594	-0.0321	-0.0585	-0.0329	-0.0200	-0.0026	-0.0010	-0.0005

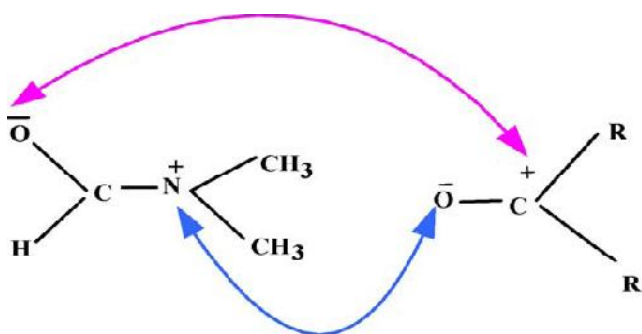
so the dipole–dipole interactions are strong; naturally they form weaker hydrogen bonds than the alkanols. Since ketones lack hydroxyl groups, they are incapable to create intermolecular hydrogen bonds, but due to the presence of oxygen, they can form hydrogen bonds with alkanol which lead to the complete solubility of low molecular weight ketones in the former solvent. The carbonyl group of ketone is polar since oxygen is more electronegative than carbon and forms a partially charged dipole.

negative excess values should be due to charge transfer and hydrogen bond formation. However, our present study shows that the increasing trend of negative values with elevation of molar concentration of alkanols in all the four system suggesting the existence of strong interaction.

DMF with alkanols mixed solvents are interesting liquid systems for studying molecular interactions, since amides and alkanols are the most common solvents used in chemical reactions and in many industrial processes. Since, DMF can interact with an alkanols by virtue of better hydrogen bond acceptor ability of its oxygen atom, resulting in structural and packing effects.

Table 4 Excess values of free volume (V_f^E) internal pressure (π_i^E) and Gibb's free energy (ΔG^{*E}) of primary alkanols with solvent mixture of DMF and MIBK at 303.15, 308.15 and 313.15 K

Mole fraction (X_1)	$V_f^E / \times 10^{-7} \text{m}^3 \text{mol}^{-1}$			$\pi_i^E / \times 10^6 \text{Nm}^{-2}$			$\Delta G^{*E} / \times 10^{20} \text{kJmol}^{-1}$		
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
1-Pentanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]									
0.0000	-0.2170	-0.2291	-0.2726	12.3243	11.1355	6.8793	0.0068	0.0140	0.0196
0.1000	-0.3115	-0.2944	-0.2818	-94.1512	-83.6851	-75.4350	0.0336	0.0467	0.0617
0.2999	-0.2415	-0.2372	-0.2140	-88.7342	-76.8584	-73.3966	-0.0007	-0.0025	-0.0308
0.4997	-0.2095	-0.1946	-0.1711	-61.5103	-57.6170	-52.3835	-0.0031	-0.0065	-0.0495
0.7000	-0.1652	-0.1574	-0.1520	-58.4131	-54.7178	-41.7096	-0.0213	-0.0272	-0.0689
0.9004	-0.1096	-0.0863	-0.0593	-20.6303	-19.9709	-17.5075	-0.0292	-0.0468	-0.0822
1-Hexanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]									
0.0000	-0.2170	-0.2291	-0.2726	12.3243	11.1355	6.8793	0.0068	0.0140	0.0196
0.0999	-0.3263	-0.2955	-0.2919	-160.0439	-99.8572	-96.4981	0.0275	0.0374	0.0468
0.2999	-0.2667	-0.2529	-0.2277	-103.9200	-85.9762	-83.3812	-0.0014	-0.0201	-0.0327
0.4998	-0.2035	-0.1531	-0.1210	-91.5970	-61.5791	-59.9163	-0.0141	-0.0298	-0.0330
0.7000	-0.1350	-0.0645	-0.0274	-59.4175	-55.5733	-45.8719	-0.0453	-0.0682	-0.0700
0.9003	-0.0886	-0.0564	-0.0109	-22.3738	-21.0344	-18.3425	-0.0778	-0.0932	-0.0969
1-Heptanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]									
0.0000	-0.2170	-0.2291	-0.2726	12.3243	11.1355	6.8793	0.0068	0.0140	0.0196
0.0999	-0.3578	-0.3042	-0.2731	-101.0727	-85.4587	-70.3331	0.0079	0.0201	0.0294
0.2999	-0.3141	-0.2601	-0.2557	-70.2967	-69.2886	-64.0159	-0.0010	-0.0176	-0.0309
0.4998	-0.2823	-0.2459	-0.1864	-63.1879	-59.2210	-54.5233	-0.0052	-0.0294	-0.0435
0.7000	-0.2081	-0.1760	-0.0928	-57.4128	-49.7226	-43.3433	-0.0270	-0.0472	-0.0516
0.9003	-0.0927	-0.0753	-0.0428	-25.4886	-24.3787	-22.7074	-0.0613	-0.0636	-0.0838
1-Octanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]									
0.0000	-0.2170	-0.2291	-0.2726	12.3243	11.1355	6.8793	0.0068	0.0140	0.0196
0.0999	-0.6158	-0.5953	-0.5554	-72.3406	-65.3138	-63.1941	0.0014	0.0067	0.0116
0.2999	-0.5784	-0.5230	-0.4647	-50.4091	-38.8183	-32.8211	-0.0037	-0.0106	-0.0275
0.4998	-0.2854	-0.2721	-0.2333	-42.7002	-27.4076	-25.3865	-0.0225	-0.0406	-0.0715
0.7000	-0.2728	-0.2583	-0.1839	-34.8061	-26.5135	-10.9437	-0.0571	-0.0686	-0.1168
0.9004	-0.1938	-0.1590	-0.0887	-22.2235	-18.8571	-9.3990	-0.0652	-0.0880	-0.1206

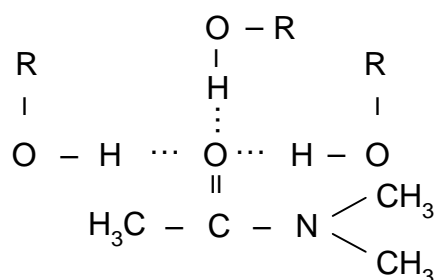


From Table 3 one can notice the variation of excess free length (L_f^E) values which are all negative over the entire mole fraction range and with the rising of temperature. According to Kannappan and Palani (1996) negative values of L_f^E indicates that sound waves cover longer distance due to decrease in intermolecular free length ascribing the dominant nature of hydrogen bond interaction between unlike molecules. Fort and Moore (1965) indicated that the positive excess value of free length should be attributed to the dispersive forces and

Due to high polar nature of DMF, which may be induced polarity in methyl isobutyl ketone and 1- alkanols and so there may be induced dipole- dipole interactions. When the compounds are mixed, the changes that occur in association equilibria are evidently rupture of hydrogen bonds in pure compounds and the formation of O-H...C=O hydrogen bonds between the components.

As alkanols are associated through hydrogen bonding, MIBK and 1-alkanol interactions are due to hydrogen bonding between the oxygen atom of the ketone and proton of hydroxyl group of alkanols. Further addition of N-N-dimethyl formamide (DMF) with the mixture causes dissociation of hydrogen bonded structure of 1- alkanols as well as leading to weak interaction between ketone and alkanols Kannappan *et al.*, (2009). The subsequent formation of new hydrogen bonding between proton acceptor of oxygen atom of $>C=O$

group of DMF and proton of $-OH$ group of 1-alkanols $>C=O \cdots H-O-$ (Ali *et al.*, 2003).



(iii) Weak physical forces, such as dipole-dipole or dipole - induced dipole interactions or Vander Waal's forces.

The factors that cause expansion in volume are the following:

- (i) Dispersion force.
- (ii) Steric hindrance of component molecules
- (iii) Unfavourable geometric fitting
- (iv) Electrostatic repulsion etc.

The negative part of V_f^E curves of the systems asserts that the combined effect of the factors responsible for volume contraction outweighs the combined effect of the factors causing volume expansion and vice-versa (Saleh *et al.*, 2002).

Table 5 Excess values of molar volume (V_m^E), and Grunberg's interaction parameter (d) of primary alkanols with solvent mixture of DMF and MIBK at 303.15, 308.15 and 313.15 K

Mole fraction (X_1)	$V_m^E / \times 10^{-3} \text{m}^3 \text{mol}^{-1}$		Grunberg's interaction parameter (d)			
			Temperature (K)			
	303.15	308.15	313.15	303.15	308.15	313.15
1-Pentanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]						
0.0000	-0.00532	-0.00536	-0.00556	0.6054	0.6929	0.7114
0.1000	-0.00071	-0.00044	-0.00022	7.1209	8.3879	9.4546
0.2999	-0.00068	-0.00040	-0.00021	2.8787	3.4443	3.9102
0.4997	-0.00065	-0.00035	-0.00019	2.3317	2.8383	3.2472
0.7000	-0.00060	-0.00032	-0.00015	2.8430	3.4569	3.9553
0.9004	-0.00046	-0.00025	-0.00014	7.1205	8.4862	9.6221
1-Hexanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]						
0.0000	-0.00532	-0.00536	-0.00556	0.6054	0.6929	0.7114
0.0999	-0.00080	-0.00071	-0.00041	7.1415	8.3872	9.4524
0.2999	-0.00033	-0.00026	-0.00016	2.8773	3.4106	3.8602
0.4998	-0.00031	-0.00021	-0.00003	2.2656	2.6828	3.0548
0.7000	-0.00020	-0.00018	-0.00002	2.8599	3.3604	3.8166
0.9003	-0.00009	-0.00008	-0.00001	7.1475	8.3795	9.4489
1-Heptanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]						
0.0000	-0.00532	-0.00536	-0.00556	0.6054	0.6929	0.7114
0.0999	-0.00098	-0.00096	-0.00087	7.1433	8.3933	9.4585
0.2999	-0.00034	-0.00030	-0.00027	2.8569	3.3782	3.8442
0.4998	-0.00031	-0.00025	-0.00020	2.4088	2.7769	3.0648
0.7000	-0.00026	-0.00020	-0.00016	2.9801	3.4974	3.9288
0.9003	-0.00022	-0.00015	-0.00006	7.1452	8.3970	9.5234
1-Octanol (X_1) + DMF (X_2) + MIBK (X_3) [$X_2/X_3 = 4:2$]						
0.0000	-0.00532	-0.00536	-0.00556	0.6054	0.6929	0.7114
0.0999	-0.00145	-0.00135	-0.00104	7.1501	8.4047	9.4233
0.2999	-0.00101	-0.00098	-0.00081	2.8777	3.4221	3.8592
0.4998	-0.00093	-0.00076	-0.00071	2.5659	3.0460	3.4444
0.7000	-0.00060	-0.00056	-0.00050	3.2123	3.8226	4.3400
0.9004	-0.00044	-0.00042	-0.00022	7.5341	8.9340	10.1290

The excess free volume indicates the extent of deviation from ideal with the mole fraction of the mixtures. The perusal of Table 4 shows that the excess values for all the four systems in the present study are found to be negative. Further these values are found to be increased with the increasing of the mole fraction of alkanols (x_1) as well as with rising of temperature. These variations can be explained in terms of molecular interaction, structural effect and interstitial accommodation along with changes in free volume. The sign of V_f^E depends upon the relative strength between the contractive forces and expansive forces. The factors responsible for volume contraction are:

- (i) Specific interaction between component molecules
- (ii) Interstitial accommodation of molecules of one component into the vacant spaces of molecules of other components. This occurs preferentially when the size difference between the component molecule is large, or when large gaps are available in the structural network of molecules.

The present increasing trends of negative excess free volume indicate the strength of the interaction between the unlike molecule increases. The observed behavior of V_f^E in the present study shows that the strength of molecular interaction is strengthened with the addition of alkanol concentration as well as with rising of temperature. Further it is also attributed that the negative contributions arise from changes of free volume in the mixtures, comprising alkanol monomer and DMF molecules, such behavior might arise from restriction of rotational motion, when the DMF molecules are accommodated interstitially with the short chain alcohols. The negative values depict that the strong hydrogen bonds formed between the -OH groups of alkanols and carbonyl (C=O) oxygen of DMF. The existence of strong hydrogen bonding (C=O...H-O) between the more polar DMF and the hydroxyl group alkanol molecules may be attributed to the presence of two unshared electron pairs on the oxygen atom of the C=O group of DMF represented by the two sp^2 -hybridized orbitals.

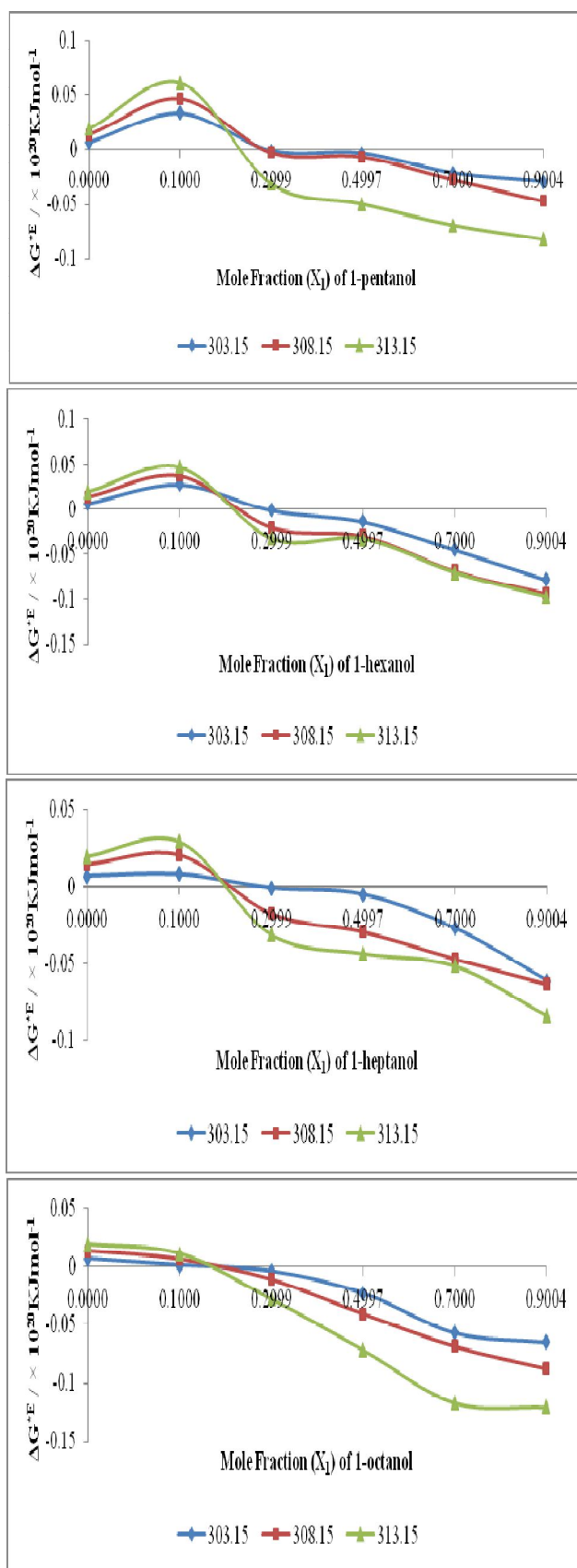


Fig. 1 Excess Gibb's free energy (ΔG^{*E}) of primary alkanols with solvent mixture of DMF and MIBK at 303.15, 308.15 and 313.15 K

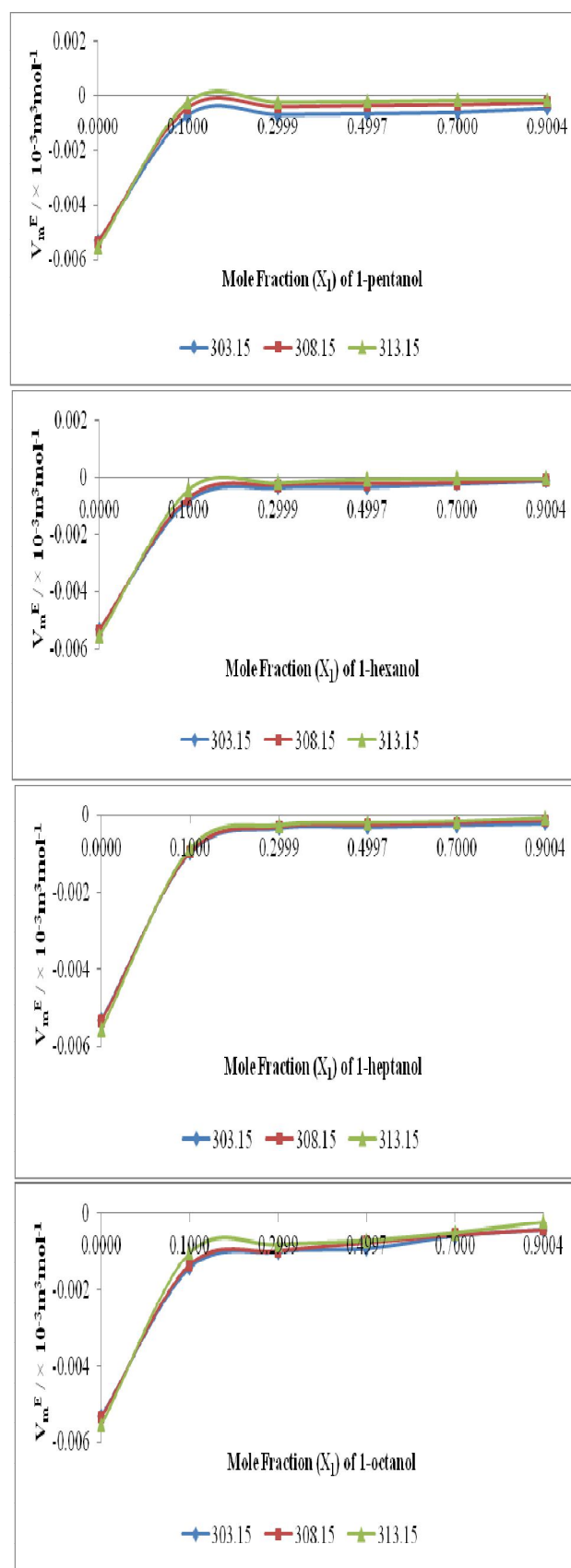


Fig. 2 Excess molar volume (V_m^E) of primary alkanols with solvent mixture of DMF and MIBK at 303.15, 308.15 and 313.15 K

In the study of liquid mixtures, the variation of internal pressure may give some reliable information regarding the nature and strength of the forces existing between the molecules. When two interacting molecules are having some sort of attractive forces like that of hydrogen bonding, they result in the increase of internal pressure. In fact, the internal pressure is a broader concept and is a measure of the totality of forces of the dispersion, ionic and dipolar interaction that contribute to be the overall cohesion of the liquid system. The present investigation shows that the excess internal pressure (π_i^E) is negative in all the four liquid systems studied and is found to be increasing with increase in mole fraction of x_1 as well as temperature too. The negative values of π_i^E indicate that dipolar forces are operating between the unlike molecules.

The present study shows that the values of excess Gibbs free energy (ΔG^E) are almost negative in all the four liquid systems studied (Fig1). However, the negative values are found to be decreased on increasing the molar concentration of primary alkanols (x_1) as well as rise of temperature. According to Reed and Taylor (1959) the positive ΔG^E may be attributed to specific interactions like hydrogen bonding and charge transfer while negative values may be ascribed to the dominance of dispersion force (Qin *et al.*, 1992). In the present investigation, it is found that the decreasing negative value of ΔG^E shows the strength of molecular interaction gets strengthened with increase of alkanols content as well as with the elevation of temperature.

The excess molar volume (V_m^E) is all negative over the entire range of concentration for the solvent mixture and primary alkanols. According to V_m^E data for ternary mixtures of DMF and MIBK with primary alkanols depends upon the balance between two opposing contributions.

(a) A positive term from the rupture of alkanol-alkanol hydrogen bonds and physical dipole-dipole interactions between alkanol monomers and multimers and

(b) A negative term from the formation of the OH π -electron hydrogen bonded complexes, changes of free volume and interstitial accommodation. The experimental data in the present investigation suggest that factor (b) which is responsible for the negative excess volume is dominant over the entire composition range in the solvent mixtures with primary alkanols. According to Awwad *et al.*, (1984) measured excess molar volume obtained in the present study can be qualitatively explained as arising due to differences in the sizes of the component molecules and in the interactions between them.

From fig 2 the values of excess molar volume for all the four liquid systems exhibit negative values and increases with elevation of molar concentration of alkanols (x_1) as well as temperature. The earlier literature survey reveals that V_m^E values are in negative with aliphatic ketones such as methyl isobutyl ketone (MIBK) with DMF and the same is positive with cyclic ketones such as cyclopentanone and cyclohexanone with DMF. The present study of possessing such negative value of V_m^E supports this. Furthermore, the

negative value of V_m^E indicate dipole-dipole interactions between the unlike molecules which leads to contraction in volume, while the positive value of V_m^E contribute to an expansion in volume. The present study of increasing value of excess free volume in all the four liquid systems confirming this prediction.

The interaction parameter (d) Grunberg and Nissan (1949), which is a measure of the strength of interaction between the component mixtures. d-values were said to indicate various types of interaction Syamala *et al.*, (2006) as follows: (a) Large and positive d-values indicate strong specific interaction and (b) Large negative values indicate no specific interaction. The present investigation suggesting that the possession of increasing positive d-values indicate specific interactions arising from the existing hydrogen bonds in the associated compounds of the mixtures. Further the increasing d-values with the elevation of temperature suggest the stronger interaction between the unlike molecules.

CONCLUSION

Ultrasonic method is a powerful probe for characterising the physico-chemical properties and existence of molecular interactions in the liquid mixtures. The evaluated ultrasonic excess values of ternary mixtures of 1-alkanols in the binary solvent mixture of DMF and MIBK (in the fixed ratio of 4:2) at 303.15, 308.15 and 313.15K which may eventually concluded that

1. The interaction between DMF (proton acceptor) and 1-alkanols is through hydrogen bonding and with MIBK through dipole-dipole interactions.
2. DMF interact with alkanols by virtue of hydrogen bond acceptor ability of its oxygen atom, resulting in structural and packing effects.
3. The further addition of DMF causes the dissociation of 1-alkanols and this leads to weak molecular interaction (hydrogen bonds) between ketone (MIBK) and 1-alkanols. Further, the elevation of temperature over the liquid mixtures leading to strengthening of their interactions.

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