



Acoustical & thermodynamic properties of some ternary systems of 1-pentanol in n-hexane solution with various organic compounds using ultrasonic technique

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The thermo-physical parameters like density, ultrasonic velocity and viscosity have been experimentally measured for the ternary liquid mixtures of 1-pentanol with N,N dimethyl formamide (N,N-DMF) / o-methoxy phenol or 2-methoxy phenol (OMP) / m-methoxy phenol or 3-methoxy phenol (MMP) in n-hexane medium at various temperatures like 303 K, 308 K and 313 K. Certain acoustical and thermodynamic parameters such as cohesive energy, available volume, viscous relaxation time, Lennard Jones potential, free energy of activation, Gibb's free energy and entropy are calculated from the experimental data. The variation of these parameters with respect to different concentrations ranging from 0.001 M to 0.01 M at different temperatures viz. 303 K, 308 K and 313 K and at fixed frequency of 2 MHz for the three ternary systems namely OMP + 1-pentanol+n-hexane, N,N-DMF+ 1-pentanol+n-hexane and MMP + 1-pentanol+n-hexane have been discussed in terms of molecular interactions under the influence of ultrasonic sound. The role of thermodynamic parameters in the stability of the charge transfer complexes and the hydrogen bonded complexes are predicted.

Keywords: Cohesive energy, Free Energy of activation, Entropy, Molecular interactions, Relaxation time

In recent years, ultrasonic investigations find extensive applications in characterisation of thermodynamic and chemical aspects of binary and ternary liquid mixtures. A third component is added to mixture of two immiscible components that bring about the disappearance of the phase boundary resulting in a homogeneous mixture. This phenomenon in certain ternary liquid mixtures has been studied earlier by observations on the distribution of molecules of one component between the other two components and by looking for the formation of hitherto unknown compounds from a study of the change in certain acoustical and thermodynamic parameters. Attempts with respect to binary/ternary systems have been made by several researchers¹⁻⁸. The thermodynamic and transport properties of multi-component systems play a vital role in calculating domains like design calculation, absorption heat pumps, heat transfer, mass transfer and fluid flow apart from the derived properties, in combination with other mixing properties, provide valuable information which may be applied to evaluate the efficiency and the predictive capability of the solution models. Process simulation, equipment design, solution theory and molecular designs are the

some of the areas where the important basic data used is density and viscosity about which the present study is dealt in addition to ultrasonic velocity⁹. In recent years more researches are being undertaken by the researchers owing to the vast applications of ultrasonic sound in the fields of medicines, pharmaceuticals, agriculture, material science, biological science including non-destructive testing and in particular the study of acoustical and thermodynamical properties of ternary liquid mixtures is being studied to know the nature of molecular interactions and packing phenomena, operating in between the atoms or molecules of the system¹⁰. This type of study is a powerful means of characterizing the various aspects of physio-chemical behaviour of ternary liquid mixtures and studying the interaction between molecules. The thermodynamic properties of mixture containing alkanols are of great industrial interest. The ultrasonic velocity value is related to binding force between atom and molecules and has been successfully used to study the nature of interactions in pure liquids, binary and ternary liquid mixtures¹¹. The variation in ultrasonic velocity value and other physical parameters are associated with weakly or strongly interacting components.

The present investigation is undertaken for three ternary systems consisting of OMP (o-methoxy phenol)/N, N-DMF (N,N dimethyl formamide) /MMP (m-methoxy phenol) + 1-pentanol in n-hexane solvent at various temperatures like 303 K, 308 K and 313 K. There are lot of differences between the branched and unbranched organic compounds, in particular alcohols and in present case unbranched C-5 (1-pentanol) is considered. The present study is focused with OMP /N,N-DMF/ MMP as donor and 1-pentanol as acceptor in n-hexane as the solvent whose dielectric constant is 1.890⁽¹²⁾. N, N-dimethylformamide (DMF) is an 'universal' solvent with the simple amide like structure. DMF has different interactions with many polymers like polyacrylonitrile, PVC, vinyl chloride-vinyl acetate co-polymer, simple organic compounds and biomolecules. It is therefore necessary to study systematically the interactions in DMF itself first. In this study, various hydrogen bonding interactions in DMF molecule based on its weak H-bonding donor CH/CH₃ and strong H-bonding acceptor C = O along with 1-pentanol are observed.

The possible H-bonding donors and acceptors in DMF molecules were analysed¹³. In o-methoxy phenol due to presence of lone pair of electron on oxygen atom exert +R effect as well as -I effect due to greater electronegativity of oxygen than carbon atoms of benzene to which it is attached. -OCH₃ group is present at ortho position with respect to -OH group, it can push electrons in to the -OH bond by +R effect. The literature survey¹⁴ reveals that electronic structures and intramolecular interactions of three methoxy phenol positional isomers and their rotamers have been studied using X-ray photoelectron spectroscopy and quantum mechanical calculations. The structural calculations are benchmarked against published calculations of enthalpy of formation and rotational constants, and published experimental data.

In addition to the above mentioned properties of organic compounds which are under study such as OMP /N,N-DMF/ MMP present in each system, the tendency of hydrogen bonding donor/acceptor character which is common among OMP, N,N-DMF, MMP along with 1-pentanol+n-hexane make interesting and stimulate the author to investigate the current study. Further, the author extends his previous study¹⁵ in different perspective. Hence, the present study has been taken by the authors to provide useful information regarding the molecular interactions

possessed in each and every system based on the acoustical and thermodynamical parameters.

Materials and Methods

The individual components present in the systems which are under study include OMP, N,N-DMF, MMP and 1-pentanol are of analytical reagent grade, Merck branded, supplied by Chandanmal traders, Chennai, India and those chemicals are once again distilled and such well purified (99.9%) substances are undertaken for the present investigation¹⁶. The solvent n-hexane (AnalaR grade) was purified by distillation and was dried over sodium wire and stored in air tight amber coloured dry bottle. The device used for the present study is ultrasonic interferometer for liquids (model F-81) supplied by Mittal enterprises, New Delhi, India and it is well calibrated by standard methods. The interferometer was calibrated using the speed of sound of water at 298.15 K. A cell with 2 MHz. frequency was used to measure the speed of sound. The cell was filled with 8 to 10 mL solution and was allowed for 30 min before taking the readings. Average of 10 readings was taken as a final value. The measured speed of sound value is accurate up to $\pm 0.05\%$. The precession of sound speed based on 10 readings was calculated as $\pm 0.02\%$. Separate temperature control water bath procured from Ragas Industries, Chennai, India is attached with interferometer. Equimolar concentrated solutions ranging from 0.001 M to 0.01 M was prepared by using the above chemicals namely OMP/N,N-DMF/MMP, 1-pentanol and n-hexane and such a well purified different concentrated solutions were allowed to pass through the interferometer at constant frequency of 2 MHz and at desired temperature under the influence of ultrasonic sound. The ultrasonic velocities of respective solutions were noted and recorded from the interferometer. Densities of the above such different concentrated solutions were measured using a single-capillary calibrated pycnometer at different temperatures such as 303 K, 308 K and 313 K. A known amount of test sample was transferred into the calibrated¹⁷ pycnometer. The pycnometer was kept for about 30 min in a thermostated water bath for minimizing the error in density with an accuracy of $\pm 0.01 \text{ kg m}^{-3}$. Similarly, the viscosities of the above different concentrated solutions at different temperatures were measured by using calibrated Ostwald viscometer. Flow time measurements were recorded in triplicate with a

digital stop watch with an accuracy of ± 0.01 s. The viscometer was kept for about 30 min in a thermo-stated water bath to minimize the thermal fluctuation in viscosity. The purification details are provided in Supplementary Data, Table S1.

Theory and calculations

Viscous relaxation time (τ) was calculated by using the standard formula²⁷. Schaafs proposed the relation for available volume (V_a) and Schaaf's limiting value is 1600 ms^{-1} for liquids. Lennard Jones Potential (LJP) was computed by using the standard relation²⁸. The cohesive energy was found out with the help of reported equations²⁹. The thermodynamic properties like free energy of activation (ΔG^*), Gibb's free energy (ΔG^0) and entropy (ΔS) were computed by using the standard formul³⁰.

Results and Discussions

Table 1 represents the observed values of ultrasonic velocity, viscosity and density for the pure components present in all the three ternary systems at working temperatures such as 303 K, 308 K and 313 K along with their corresponding literature values. The experimentally measured values of ultrasonic velocity, viscosity and density for the mixtures (OMP/N,N-DMF/MMP +1-Pentanol + n hexane) at 303 K, 308 K and 313 K were presented in Tables 2, 3 and 4, respectively.

Role of available volume (V_a)

The available volume is the direct measure of compactness and the strength of binding forces between the molecules of a liquid mixture. In our present study the values of available volume for OMP

Table 1 — Observed values of ultrasonic velocity (u), viscosity (η) and density (ρ) for the pure components present in three ternary systems at working temperatures

Value	Component	$u \text{ (m s}^{-1}\text{)}$			$\eta \text{ (N s m}^{-2}\text{)} \times 10^{-4}$			$\rho \text{ (kg m}^{-3}\text{)}$		
		303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
Observed Literature	n-Hexane	1076.1	1054.4	1032.4	0.320	0.317	0.301	651	648	647
		1058.3	NA	NA	0.296	NA	NA	651	NA	NA
		[18]			[24]			[23]		
Observed Literature	1-Pentanal	1280.0	1250.4	1200.5	2.798	2.720	2.426	886	883	865
		1280.5	NA	1189.1	2.771	NA	2.381	802	NA	787
		[19]		[20]	[21]		[22]	[21]		[22]
Observed Literature	OMP	1683.2	1560.8	1227.6	4.290	4.176	3.876	1080	1076	1078
		1509.3	1490.0	1470.7	4.435	NA	NA	1124	1119	1114
		[25]	[25]	[25]	[25]				[25]	[25]
Observed Literature	N,N-DMF	1370.8	1345.2	1201.6	0.988	0.808	0.654	965	963	958
		1382.8	1371.7	1360.7	0.667	0.529	0.437	1293	1289	1285
		[26]	[26]	[26]	[26]	[26]	[26]	[26]	[26]	[26]
Observed Literature	MMP	1563.2	1440.8	1332.1	2.424	1.924	1.299	1080	1077	1080
		NA	NA	NA	NA	NA	NA	NA	NA	NA

Standard uncertainties u_r are $u_r(T) = \pm 0.1 \text{ K}$, $u_r(\rho) = \pm 0.5 \text{ kg m}^{-3}$, $u_r(\eta) = \pm 0.02 \text{ N s m}^{-2}$, $u_r(u) = \pm 0.5 \text{ m s}^{-1}$.

The references are given square brackets, NA-not available

Table 2 — Experimental values of ultrasonic velocity (u), viscosity (η) and density (ρ) for OMP/N,N-DMF/MMP+1-Pentanol+n-Hexane at 303 K

Conc. (M) $\times 10^{-3}$	$u \text{ (m s}^{-1}\text{)}$			$\eta \text{ (N s m}^{-2}\text{)} \times 10^{-4}$			$\rho \text{ (kg m}^{-3}\text{)}$		
	OMP	N,N-DMF	MMP	OMP	N,N-DMF	MMP	OMP	N,N-DMF	MMP
1	1080.88	1044.00	1182.81	5.515	4.635	5.378	791.7	806	861.1
2	1064.12	1046.10	1186.91	5.446	4.644	5.507	788.9	806	861.1
3	1055.78	1047.83	1188.41	5.382	4.695	5.414	794.0	806	863.2
4	1050.05	1049.16	1187.51	5.368	4.704	5.258	788.3	806	863.2
5	1063.22	1051.13	1189.72	5.416	4.708	5.558	788.3	806	862.3
6	1070.00	1052.12	1189.22	5.350	4.726	5.565	786.1	807	860.1
7	1075.22	1053.66	1190.52	5.343	4.747	5.480	787.7	807	861.1
8	1077.45	1054.72	1191.31	5.477	4.765	5.349	786.5	807	862.1
9	1077.51	1055.63	1195.22	5.316	4.792	5.576	786.5	808	862.2
10	1083.15	1056.80	1198.91	5.317	4.813	5.591	788.3	808	862.2

Table 3 — Experimental values of ultrasonic velocity (u), viscosity (η) and density (ρ) for OMP/N,N-DMF/MMP+1-Pentanol+n-Hexane at 308 K

Conc. (M) $\times 10^{-3}$	u (m s ⁻¹)			η (N s m ⁻²) $\times 10^{-4}$			ρ (kg m ⁻³)		
	OMP	N,N-DMF	MMP	OMP	N,N-DMF	MMP	OMP	N,N-DMF	MMP
1	1039.92	1029.16	1105.11	5.050	4.74	5.543	786.4	801	858.1
2	1042.12	1029.72	1110.52	5.107	4.75	5.550	785.5	801	858.2
3	1040.58	1030.15	1115.22	5.079	4.77	5.577	784.1	801	860.2
4	1042.61	1031.08	1118.11	5.143	4.78	5.579	785.3	801	860.2
5	1041.49	1031.33	1120.63	5.322	4.87	5.744	785.5	801	860.3
6	1039.55	1032.73	1124.73	5.116	4.91	5.758	786.4	801	860.4
7	1041.56	1032.89	1128.22	5.152	4.92	5.796	786.4	802	860.3
8	1040.00	1033.25	1128.92	5.141	4.95	5.847	786.4	802	861.2
9	1044.74	1034.62	1130.41	5.130	4.97	5.862	785.3	802	861.1
10	1044.65	1034.88	1131.51	5.145	5.01	5.891	786.4	802	862.1

Table 4 — Experimental values of ultrasonic velocity, viscosity and density for OMP/N,N-DMF/MMP+1-Pentanol+n-Hexane at 313 K

Conc. (M) $\times 10^{-3}$	u (m s ⁻¹)			η (N s m ⁻²) $\times 10^{-4}$			ρ (kg m ⁻³)		
	OMP	N,N-DMF	MMP	OMP	N,N-DMF	MMP	OMP	N,N-DMF	MMP
1	1012.95	1010.80	1016.62	5.196	5.03	5.880	788.2	798	856.1
2	1013.96	1011.14	1017.12	5.198	5.04	6.012	788.7	798	857.2
3	1015.44	1011.68	1019.02	5.278	5.06	6.101	789.9	798	858.4
4	1013.20	1012.28	1022.83	5.160	5.10	6.141	788.7	798	858.2
5	1015.63	1012.93	1023.53	5.204	5.15	6.165	789.3	798	859.2
6	1013.61	1013.17	1026.94	5.300	5.18	6.154	788.7	798	860.1
7	1014.40	1013.29	1028.41	5.228	5.19	6.221	787.0	799	860.2
8	1013.51	1013.43	1030.71	5.141	5.21	6.280	785.3	799	860.3
9	1015.68	1013.58	1031.22	5.299	5.26	6.290	789.9	799	860.2
10	1014.68	1013.66	1033.61	5.228	5.32	6.314	787.0	799	861.2

mixture is higher than the corresponding MMP mixture at all the working temperatures for all the concentrations. This shows that the interaction becomes weak for OMP when compare with MMP which is due to the presence of steric effect in OMP ternary system and as expected the interaction level is medium for N,N-DMF mixture i.e., in between OMP and MMP. The readings are tabulated in Supplementary Data, Tables S2, S3 and S4 and plotted in Fig. S1.

Role of Lennard jones potential (LJP)

The LJP is a mathematically simple model that approximates the interaction between the pair of neutral atoms or molecules in a mixture. The decrease in LJP values with increase of temperature shows that the extent of complexation decreases with increase of temperature in all the three ternary liquid systems. The values are represented in Supplementary Data, Tables S2-S4 and the plots are shown in Fig. S2. The decrease in LJP value with raise in temperature shows again the interaction between the components in all the systems decreases due to net packing of molecules inside the shell because of complexation between unlike molecules through hydrogen bonding. LJP

represents the energy of repulsion decreases. These observations revealed the complex formation takes place between OMP/ N,N-DMF/ MMP and 1-pentanol in n-hexane medium.

Role of viscous relaxation time

Relaxation time and absorption coefficient are directly related. The absorption of sound wave is the result of time lag i.e., relaxation time between the passing of the ultrasonic wave and the return of the molecules to their equilibrium position. For a material with a low absorption coefficient, light is poorly absorbed. The relaxation time and free energy of activation ΔG^* are intrinsic properties of charge transfer complex and the values are almost constant at different concentrations. The plots between concentration and viscous relaxation time are shown in Fig. 1 for all the three systems at 303 K, 308 K and 313 K. From these plots, it can be concluded that same type of result is obtained in our present study. This means that the values do not significantly change at given temperature for all the three systems at 303 K, 308 K and 313 K. This suggests that similar type of interaction is noticed in all the ternary liquid systems at different temperatures. The

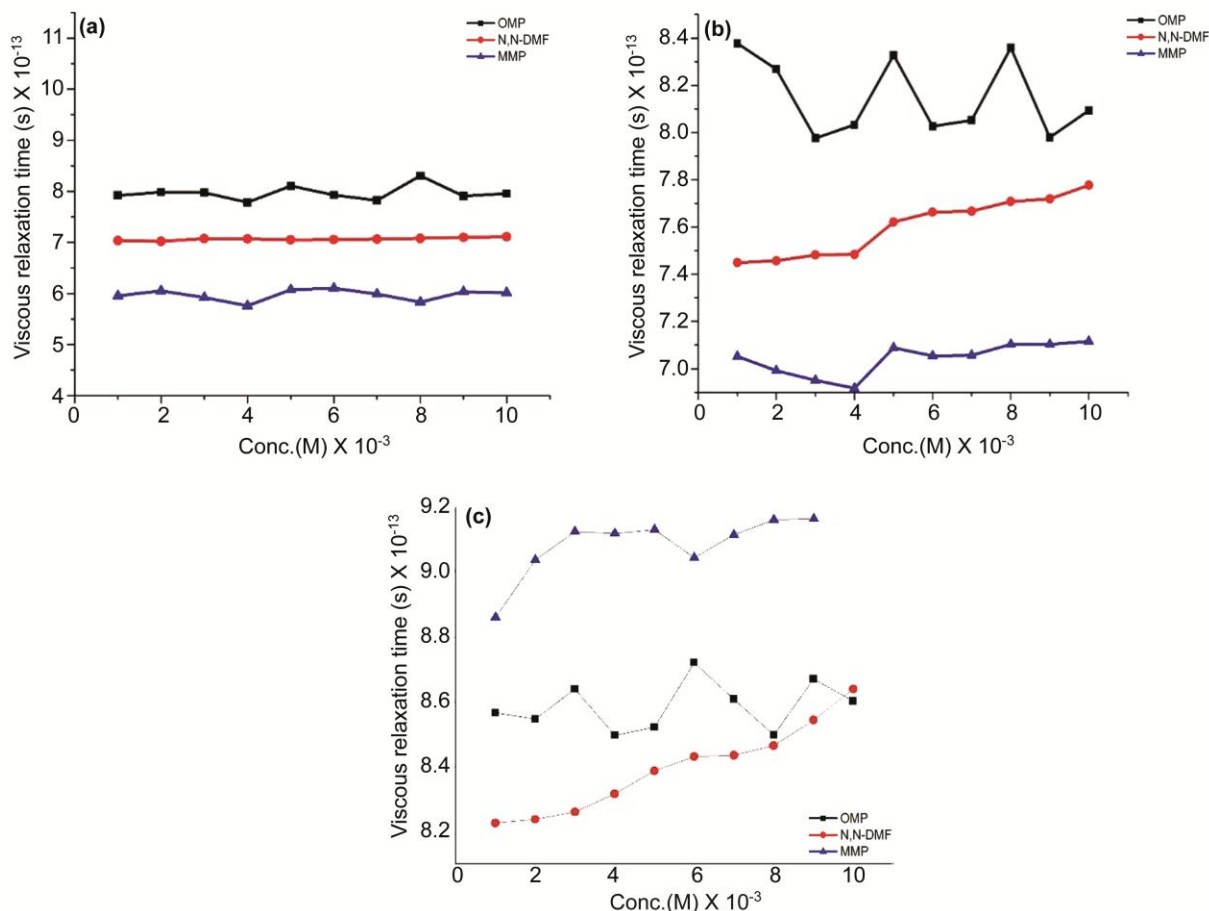


Fig. 1 — Plots between Conc.(M) and viscous relaxation time for OMP/N, N-DMF/MMP+1-Pentanol+n Hexane at (a) 303 K, (b) 308 K and (c) 313 K

values are provided in Supplementary Data, Tables S5, S6 and S7.

Role of cohesive energy

Cohesive energy in liquid mixture is a measure of the molecular interaction between the components. If the cohesive energy values are small, the intermolecular forces are weak due to which chains are relatively flexible. A molecule with strong polar groups will exert strong attractive forces on its neighbours. The plots between concentration and cohesive energy are shown in Fig. 2 for all the three systems at 303 K, 308 K and 313 K. In the present study, the cohesive energy values increase with increase in temperature for the ternary systems N,N-DMF/ MMP show the presence of weak interaction is observed at high temperature. These observations revealed the complex formation takes place between N, N-DMF/MMP and 1-pentanol in n-hexane solvent. This is due to weak induced dipole-induced dipole is stronger. The same trend is observed

by Kannappan *et al.*³¹. But at the same time, in our present study, the values of cohesive energy decreases in the ternary liquid mixture OMP and 1-pentanol in n-hexane with increase of temperature. This shows that the interaction decreases with increase of temperature. The values are provided in Supplementary Data, Tables S5, S6 and S7.

Role of free energy of activation (ΔG^*)

From the literature study, it is understood that there is a certain degree of association in the pure components due to hydrogen bond formation and these associations are broken down on formation of mixture. There will be three types of interactions namely the attractions due to van der Waals forces, dipole-induced dipole attractions and hydrogen bonded interactions. Generally, in ternary systems fewer interactions are reported because the addition of third component decrease the energy of interaction and the system behaves as ideal ones. The chemical reactions (interactions) may not take place due to one

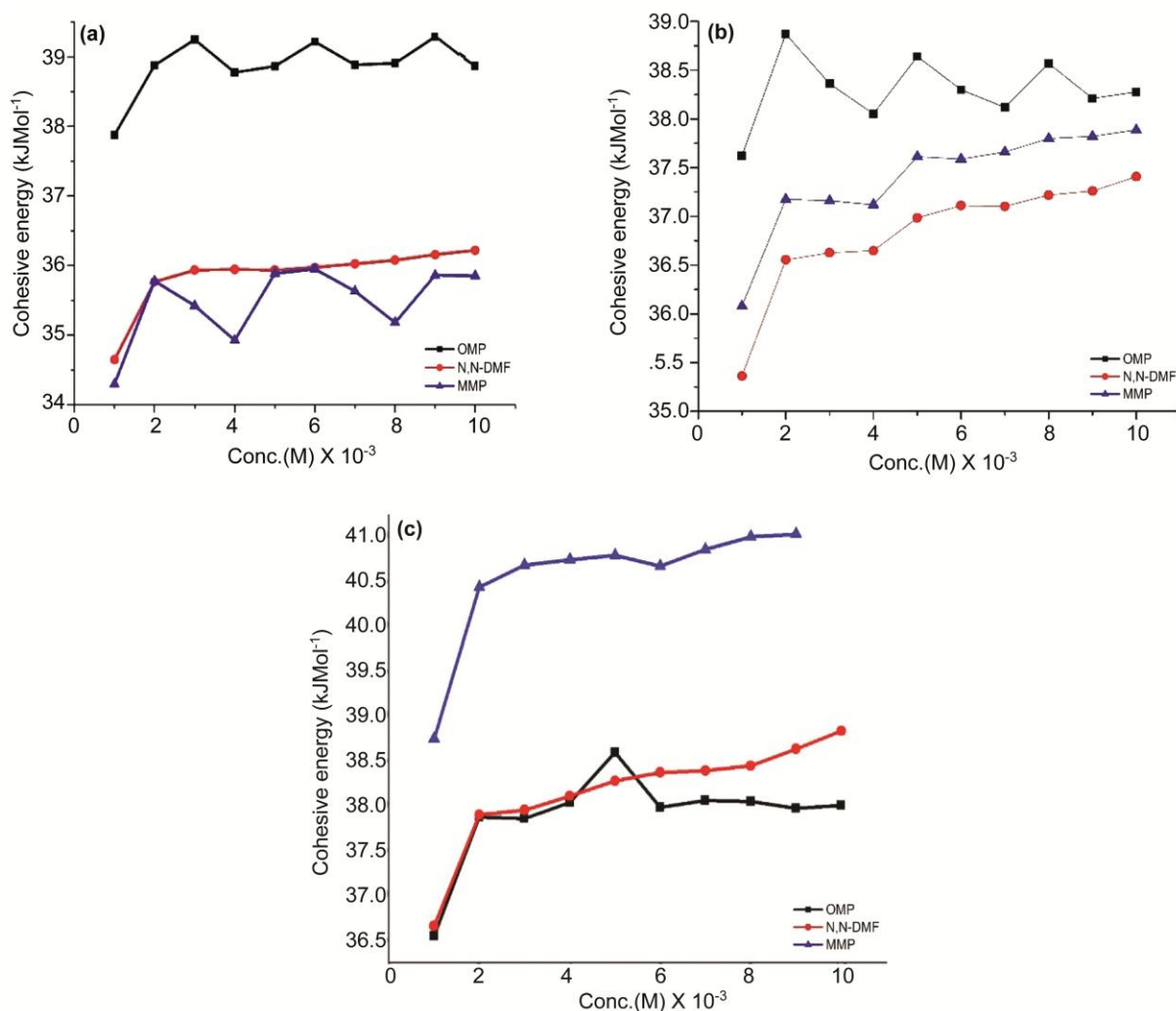


Fig. 2 — Plots between Conc.(M) and Cohesive energy for OMP/N, N-DMF/MMP+1-Pentanol+n Hexane at (a) 303 K, (b) 308 K and (c) 313 K

of the reasons is, the reactants do not collide with the right geometry i.e. there is steric hindrance and it is further come to understand that the aromatic derivatives set up an interaction between π electron cloud and hydroxyl group (Stokes and Robinson, 1982). Though the interaction is of minor intensity compared with hydrogen bonding but they lead to the formation of intermolecular complexes (Prigogine, 1937). The plots between concentration and ΔG^* are shown in Fig. 3 for all the three systems at 303 K, 308 K and 313 K. The values are depicted in Supplementary Data, Tables S8, S9 and S10. Hence in this present investigation, the steric hindrance is exhibited in the OMP system due to which the interactions are weak, this may be further supported by the values of cohesive energy but due to the formation of inter-molecular hydrogen bonding along

with 1-pentanol, there is an appreciable change in the nature of the interactions which may be indicated by the positive values obtained for ΔG^* at all the working temperatures irrespective of all the concentrations. The literature survey reveals the determination of ΔG° (XH) values of many important organic hydride donors and the ΔG° (Y+) values of many important organic hydride acceptors, such as olefins, imines and carbonyl compounds in acetonitrile at room temperature. The effects of substituents on the free energies of activation ΔG^* of H-bond donor/acceptor reactions are generally quite small (smaller than 1 kcal mol^{-1}), except the substituent at the position of the reaction centre where both electron withdrawing and electron-donating substituents significantly increase the free energies of activation. This statement is supported by the present

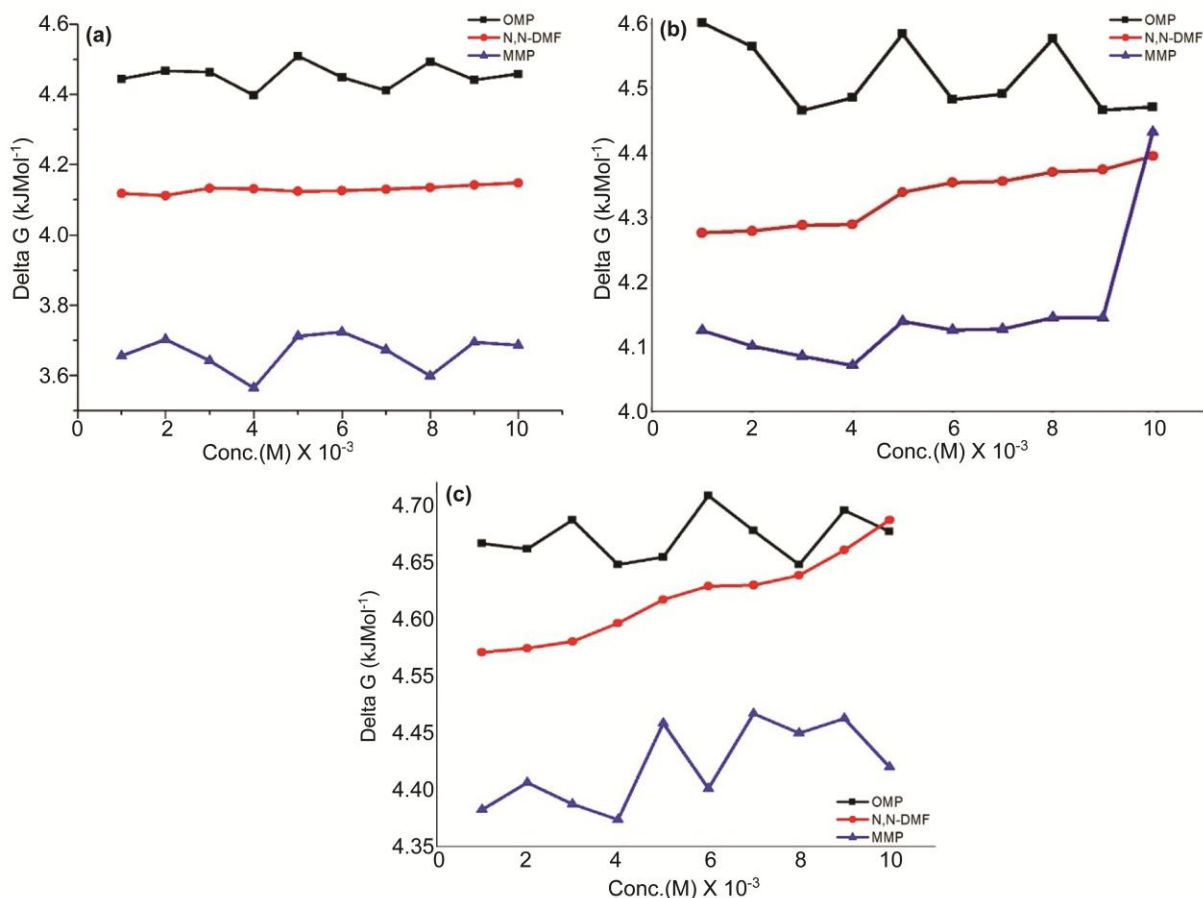


Fig. 3 — Plots between Conc.(M) and ΔG^* for OMP/N, N-DMF/MMP+1-Pentanol+n Hexane at (a) 303 K, (b) 308 K and (c) 313 K

study. In this present probe, the values of ΔG^* for all the three systems at all the three temperatures irrespective of concentrations, are found to be more or less closer to each other except for the system OMP + 1-pentanol in n-hexane solvent at 303 K wherein the values are in the range of 3.6-3.7 kJ Mol⁻¹ and those values are observed to be possessing very least deviation when compared with rest of the values. The reason for this behaviour is due to the slight rupture of intramolecular hydrogen bonding in OMP. The focus of the present investigation is study the effect of increasing chain length of 1-pentanol on the strength of the H-bonding between phenolic ethers (OMP/MMP) and N,N-DMF and aliphatic alcohol. This can be quantitatively assessed by the determination of formation constant (K), free energy of activation (ΔG^*), Gibbs free energy change (ΔG^0) and entropy change (ΔS) for the formation of the hydrogen bonded complexes. The equilibrium constant for the formation of 1:1 stoichiometric complex can be calculated from the ultrasonic

velocity using the Kannappan equation³². It has been used for the formation of several charge transfer and hydrogen bonded complexes.

Role of Gibbs free energy (ΔG^0)

In chemical thermodynamics, the term used for the chemical potential energy is chemical potential, and for chemical transformation, an equation most often used is Gibbs - Duhem equation or Gibbs equation. G depends on various extensive compositional variables $\{N_i\}$ which specify the composition, the amount of each chemical substance, expressed on the numbers of molecules present or the number of moles (dividing by Avogadro's number) as per the following equations,

$$G = G(T, P, \{N_i\}) \quad \dots (1)$$

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right) T, P, N_j \neq i, \text{ etc.} \quad \dots (2)$$

where μ_i is the chemical potential for the i^{th} component in the system.

In order to represent degree of advancement of process, a progress variable ϵ and to the use of partial

derivative (in place of widely used ΔG^*) and for a single reaction,

$$dG = \left(\frac{\partial G}{\partial \epsilon}\right)T, P(d\epsilon) \quad \dots (3)$$

In solution chemistry, the Gibbs free energy (ΔG^*) decrease is commonly used as a surrogate for (-T times) the entropy produced by spontaneous chemical reactions in situations where there is no work being done; or at least no useful work i.e., other than perhaps some $\pm Pdv$. The assertion that all spontaneous reactions have a negative is merely a restatement of the fundamental thermodynamic relation, giving it the physical dimensions of energy and somewhat obscuring its significance in terms of entropy when there is no useful work being done. In this present study, it is observed that the magnitude of ΔG^0 decreases at all the temperatures for all the three systems while the concentration increases. Also with the increase in temperature, the magnitude of ΔG^0 decreases for all the three systems. Also it is noted that the magnitude of ΔG^0 is higher for MMP at particular temperature irrespective of concentration than that of OMP; there is no appreciable change in between OMP and N,N-DMF with respect to the magnitude of ΔG^0 . Further for all the three systems, negative values are recorded. The values are depicted in Supplementary Data, Tables S8 – S10. The plots of ΔG^0 values with concentration are shown in Supplementary Data, Fig. S3. The sign of the values like ΔG^0 & ΔS play a vital role in determining the thermodynamic properties. It is inferred that a strong molecular interaction is possible because of the negative values which is mainly due to intermolecular/intramolecular hydrogen bonding, dipole-dipole interaction between OMP/N,N-DMF/MMP and 1- pentanol & dipole-induced dipole between OMP/N, N-DMF/MMP and n hexane and it is further noted that due to electron releasing effect exhibited by the MMP, the interaction will be comparatively strong in this system. ΔG^0 decreases with increase in temperature at all concentrations for all the three systems is due to increase in kinetic energy which is caused by increase in thermal agitation of the molecule at given concentration³³⁻³⁵.

Role of entropy (ΔS)

Decomposition of the total binding free energy as shown in the following equation emphasizes that the entropy of binding is comprised of contributions from the donor like OMP/N,N-DMF/MMP, the acceptor 1-pentanol and the solvent n-hexane:

$$\Delta G_{tot} = \Delta H_{tot} - T\Delta S_{tot} = \Delta H_{bind} - T(\Delta S_{donor} + \Delta S_{acceptor} + \Delta S_{solvent}) \quad \dots (4)$$

The contributions by solvent entropy have taken centre stage and are usually framed in terms of the so-called hydrophobic effect. In principle, the entropic contributions of a donor to the binding of the acceptor include both changes in its internal conformational entropy (ΔS_{conf}) as well as changes in rotational and translational entropy (ΔS_{RT}). In this present study, it is observed that the magnitude of ΔS decreases at all the temperatures for all the three systems while the concentration increases (except at 313 K for 0.002 M). But when the temperature increases, the magnitude of ΔS decreases slightly for all the three systems. Also it is noted that the magnitude of ΔS is slightly higher for MMP at particular temperature irrespective of concentration than that of OMP; there is no appreciable change in between OMP and N,N-DMF with respect to the magnitude of ΔS . Further for all the three systems, negative values are recorded. As a complete study regarding the values of ΔS , it is found that there is no larger deviation among all the three systems at all the working temperatures irrespective of concentrations. The values are depicted in Supplementary Data, Tables S8 – S10. The plots of ΔS values with concentration are shown in Supplementary Data, Fig. S4. The ΔS values (magnitude alone) clearly reveals that the gradual increase in concentration at all the working temperatures causes decrease in entropy which is originally degree of randomness and hence eventually at higher concentration, the molecules closely packed i.e., decrease in randomness and this point is evident from the values obtained for ΔS in the present study. It has been understood also that at all the concentrations for all the three systems, the increase in temperature paves the way for disruption in association between the molecules which is caused because of thermal agitation at higher temperatures but it is seen that this increase in temperature do not possess sufficient energy to disturb a lot in their molecular associations. It may be also seen that the hydrogen of alcohol may be accepted by either ethereal oxygen or oxygen of -OH in case of OMP & MMP group / weak H- bonding acceptor tendency of C=O in case of DMF. Thus, the formation of H-bonded complexes in these three systems are also supported by the negative entropy values. Further, these H-bonded complexes are thermodynamically stable as indicated by the negative ΔG^0 values for all

the complexes. Constant relaxation values for the three complexes indicate that similar type of complex is formed in all the three systems. Entropy change values are computed from the K values (which are provided in Tables S2, S3 & S4) at three different temperatures using thermodynamic relations. It has been reported that 1-alkanols form H-bonded complexes with cyclohexanone in dimethylacetamide (DMA) and the order is reported as 1-propanol >1-pentanol>1-butanol. The reason for the reverse in 1-butanoland 1-pentanol is given as due to the proton abstracting ability of DMA³⁶⁻³⁹. But in the present work, non-polar n-hexane medium is used and hence the role of solvent on the stability of the complex is negligible. Therefore, it may be concluded that the strength of the hydrogen bond in these complexes decreases with increase in chain length. It is found that the entropy change for the formation of complex is negative in all the three systems indicating that the orderliness increases during the formation of the complex.

Conclusions

Ultrasonic studies are made on three ternary systems containing OMP + 1-pentanol+n-hexane, N,N-DMF+1-pentanol+n-hexane and MMP+ 1-pentanol+n-hexane at three different temperatures such as 303 K, 308 K and 313 K. The variation in certain acoustic properties which are under probe with concentration at a given temperature establishes the existence of interactions such as dipole-dipole, dipole-induced dipole, induced dipole-induced dipole in addition to specific interaction (H-bonded attraction). Thermodynamic properties such as free energy of activation (ΔG^*), Gibbs free energy (ΔG^0) and entropy change (ΔS) (for the complex formation) are determined. These parameters are used to assess the stability of complexes and to study the influence of chain length of the alcohol on the stability of the complex. Negative values of ΔG^0 & ΔS show that these complexes are thermodynamically stable. The formation of these complexes is exothermic as evident and as predicted from the negative values but in contrast, additional interactions of interstitial accommodation undergo an overall decrease in ΔG^* making the process markedly endothermic as a whole at 303 K, 308 K and 313 K. These complexes have similar type of interaction as shown by the constant relaxation time values for the three systems. Thus increase in chain length of 1-alkanol decreases the stability. The positive values recorded for ΔG^* predict

the strong interactions between the components which paves the way for formation of strong complexes.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at [http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A\(07\)943-952_SupplData.pdf](http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(07)943-952_SupplData.pdf).

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