Excess Properties and Theoretical Evaluation on Ternary Systems of 1-Pentanol in n-Hexane Solution with some Organic Compounds at 313 K Using Ultrasonic Technique

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Abstract: The parameters like density(ρ), ultrasonic velocity (U), and viscosity (η) were experimentally measured. The excess parameters like adiabatic compressibility, acoustic impedance, free volume, free length, internal pressure and ultrasonic velocity in addition to K value were computed from the experimental data. The variation of these parameters at a constant temperature 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 the light of molecular interaction. Further, certain theoretical studies are validated with respect to experimental velocities, and the Chi-square test for the goodness of fit is also applied to check the validity of such theoretical models.

Keywords: Charge-transfer complex, stability constant, excess acoustic impedance, Chi-square, molecular interactions.

1. INTRODUCTION

Ultrasonic studies play a vital role in various fields such as medicinal, biological, food industries, pharmaceuticals, Non-destructive testing (NDT) and molecular liquids, etc. Through the ultrasonic studies of liquid mixtures, which are of micro-level concentrations, the strength or nature of the molecular interactions can be detected and assessed [1, 2]. The ultrasonic velocity is temperature dependant for most of the liquid mixture with respect to their acoustical properties. The present investigation is undertaken for three ternary systems consisting of OMP (o (2)-methoxy phenol) /N, N-DMF (N, N dimethylformamide) /MMP (m (3)-methoxy phenol) + 1-pentanol in n-hexane medium at constant temperature 313 K. The organic compounds which are considered for the present study such as OMP, N, N-DMF, and MMP are used in a wide variety of reactions including electrophilic substitution, nucleophilic substitution, oxidation and reduction [3]. n-hexane may not be able to deprotonate under normal temperature, but at high temperature, its behaviour is changed, and hence it is used in various fields like separation technique, preparation of organolithium, etc. For the preparation of many organic compounds, the role of alcohol is considered as important. There are many differences between the branched and unbranched organic compounds, particularly alcohols, and in the present case, unbranched C-5 is considered [4]. The present study is undertaken with OMP /N, N-DMF/ MMP as a donor, and 1-pentanol as an acceptor in n-hexane as the

solvent. The present study doesn't consider the para substituent (para methoxy phenol) since it is deliquescent in nature, and also, the instrument which is used in the present investigation is specially made for liquids alone. Besides, the following characters of the organic compounds which are under study prompted the author to probe the present study.

The radical scavenging activity and cytotoxicity of 2-methoxy phenols(OMP) and related compounds and their effect on lipopolysaccharide (LPS) gives rise to possess the antioxidant property. 2-Methoxy phenols are antioxidants widely used in the cosmetic and food industries. Dimers were synthesized, and their radical-scavenging and biological activities were compared with those of the original or other phenols. Computational chemistry is one of the most rapidly expanding and exciting areas of scientific endeavour in the medical, dental, and material sciences [5-21]. The information available from computational methods may help interpret the molecular mechanism of interactions of 2- methoxy phenol antioxidants. N, N-DMF is used in the synthesis of many organic compounds like 2 nitroso 5 methoxy phenol, which is used in the medicinal field, and the same N, N-DMF is also used as food additives and colourants. It is understood that the role of N, N-DMF as in pharmacology and in biochemical reactions which itself a predicted metabolite found in the human body; MMP is used as a food additive, and flavouring agent including cosmetics, perfumes, lotion, shampoos, toothpaste, etc. and these characters of organic compounds (OMP, N, N-DMF, and MMP) stimulated the author to undertake the present study [22, 23].

Therefore, the authors have taken the present study to provide useful information regarding the molecular

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interactions possessed in each and every system, and a comparison is made with respect to their interactions. Moreover, theoretical ultrasonic velocities based on theories such as Van Dael Ideal Mixing Relation(IMR), Impedance Dependent Relation(IMP), Junjie's (JUN), and Nomoto's (NOM) relations are validated with experimental velocities for all the three systems [system I=OMP+1-pentanol +n-hexane; system II=N, N-DMF+1-pentanol +n-hexane; system III=MMP+1-pentanol+n-hexane] at all the ten equimolar concentrations at 313 K. To make the present investigation, more reliable, consistent and accurate, the theoretical findings are suited with Chi-square test for the goodness of fit.

2. EXPERIMENTAL

2.1. Materials

The mixtures (1-pentanol + OMP/N, N-DMF/MMP +n-hexane) of various concentrations ranging from 0.001 M to 0.01 M of all the three systems, namely OMP+ 1-pentanol +n-hexane, N, N-DMF+ 1-pentanol +n-hexane, and MMP+ 1-pentanol+n-hexane, were prepared by taking analytical reagent grade and spectroscopic reagent grade chemicals with the minimum assay of 99.9% and procured from E. Merck Ltd. (India) (Table **1**).

2.2. Methods

All the component liquids were purified by the standard methods [24]. The density, viscosity, and ultrasonic velocity were measured for various concentrations viz. 0.001-0.01 M of all the three systems at a constant temperature of 313 K, keeping the fixed frequency of 2 M Hz. Ultrasonic velocity measurements were taken using an ultrasonic interferometer (Model F-81, supplied by M/S Mittal Enterprises, New Delhi) with an accuracy of $\pm 0.1 ms^{-1}$. Water at the desired temperature of 313 K is circulated through the outer jacket of the double-walled measuring cell of the interferometer containing the experimental ternary liquid mixture. The densities of the mixture were measured using a 10 ml specific gravity bottle by the relative measurement method with

an accuracy of $\pm 0.01 \ kgm^{-3}$. An Oswald viscometer (10 ml) with an accuracy of $\pm 0.001 \ Nsm^{-2}$ was used for the viscosity measurement. The flow time was determined using a digital racer stopwatch with an accuracy of $\pm 0.1s$.

3. THEORY AND CALCULATIONS

3.1. The Values of Acoustical (Normal) Properties and Thermodynamic Properties are Calculated or Computed by Using Standard Formulae

The values of U^E, Z^E, and L_f^E for each mixture have been fitted to the Redlich –

Kister polynomial equation [25]

$$Y^E = x(1-x)\sum_{i=1}^{10} a_i (1-2x)^{i-1} \tag{1}$$

The values of the coefficients a_i were calculated by the method of least squares along with the standard deviation $\sigma(Y^E)$. The coefficients i is an adjustable parameter for the best fit of the excess functions.

$$\sigma(Y^E) = \left[\frac{\Sigma(Y_{expt}-Y_{cal})}{n-p}\right]^{1/2} \tag{2}$$

where n is the number of experimental points, p is the number of parameters, and Y_{expt} and Y_{cal} are the experimental and calculated excess parameters.

3.2. Theoretical Studies

The following theoretical relations were compared with the experimental values of ultrasonic velocity.

Nomoto's Equation [26]:

$$U_{NR}= \sum_{i=1}^{n} \frac{xiRi}{xiVmi} \tag{3}$$

Van Dael Ideal Mixing Relation [27]:

$$U_{IMR} = \left(\sum_{i=1}^{n} xiMi\right)^{1/2}\left(\sum_{i=1}^{n} \frac{xi}{MiV_{Mi}^2}\right)^{1/2} \tag{4}$$

Junjie's Relation [28]:

$$U_{JR} = \left(\sum_{i=1}^{n} xiVmi\right)\left(\sum_{i=1}^{n} xiMi\right)^{1/2}\left[\frac{\sum_{i=1}^{n} xiVmi}{\sum_{i=1}^{n} \rho iU_i^2}\right]^{1/2} \tag{5}$$

Table 1:   CAS Registry and Procurement Particulars

Sl. No.	Name of the component	CAS RN	Supplier's Name	Brand Name
1	n-Hexane	110-54-3	Chandanmal and Co., Chennai, India.	E. Merck Ltd (India)
2	1-pentanol	71-41-0		
3	N, N–Dimethylformamide (N,N-DMF)	68-12-2		
4	2 Methoxy Phenol or o. methoxy phenol (OMP)	90-05-1		
5	3 MethoxyPhenolor m. methoxy phenol (MMP)	150-19-6		

Impedance Dependent Relation [29]:

$$U_{IMP} = \frac{\sum_{i=0}^{n} x_i \rho_i U_i}{\sum_{i=0}^{n} x_i \rho_i} \tag{6}$$

Where x_i is Mole fraction, R_i is molar sound velocity, ρ_i is the density, and V_{mi} is the molar volume.

Absolute Average Percentage Deviation (AAPD) = $\frac{1}{n} \sum \left[\frac{(U_{exp} - U_{the})}{U_{exp}} \right] \times 100 \tag{7}$

% Error (PE) = {$(U_{exp} - U_{the})/U_{exp}$}X100 (8)

Where U_{exp} is the experimental ultrasonic velocity, and U_{the} is the theoretical ultrasonic velocity.

Degree of Molecular Interaction (DMI) Parameter α = $(U^2_{exp} / U^2_{ideal}) - 1 \tag{9}$

Where U_{ideal} is ideal mixing velocity

The linear or non-linear behaviour of the systems can be determined by the following relation.

$$NI = (U^2_{exp} / U^2_{ideal}) \tag{10}$$

3.3. Statistical Analysis and Stability Constant

According to Pearson [30], the Chi-square test for the goodness of fit is given by

$$|\chi^2| \text{Chi-square} = \sum_{i=1}^{n} \left[\frac{(U_{exp} - U_{the})(U_{exp} - U_{the})}{U_{the}} \right] \tag{11}$$

The stability constant K [31-33], is given by

$$K = Y/(b-y)^2 \tag{12}$$

$Y = (a - k^{1/2}b) / (k - k^{1/2})$ in which k = x/y, x is the difference between U_{cal} and U_{obs} at lower concentration a, y is the difference between U_{cal} and U_{obs} at higher concentration b, U_{cal} is the ultrasonic velocity of the mixture calculated from the mole fraction of the components using additive principle.

4. RESULTS AND DISCUSSION

4.1. Experimental Determination of Velocity, Viscosity and Density and the Tabulation for the Excess Properties, Theoretical Studies, and Chi-Square Test

The molecular interactions among the constituent substances are studied under the influence of ultrasonic waves over the mixture of solutions [34]. These molecular interactions are decided based on the factors involving dipole-dipole, dipole-induced dipole, nature of hydrogen bonding, and the formation of a charge-transfer complex. The normal acoustical properties will not provide high précised results; instead, excess properties envisage the accurate

results because the present investigation is dealt with ultra- micro-level concentrations of the ternary system of the liquid mixture. And of course, in the present study, the values of excess properties like Z^E, π_i^E, β^E, L_f^E, U^E and V_f^E are computed from the calculated acoustical properties, which are based on the experimental ultrasonic velocity, viscosity, and density, and those values are tabulated in Table **2**. The findings of calculated acoustical properties such as adiabatic compressibility(β), absorption coefficient (α/f^2), internal pressure(π$_i$), cohesive energy(CE), free volume(V$_f$), free length(L$_f$), acoustic impedance(z), available volume(V$_a$), viscous relaxation time, ΔG value, Lenard Jones potential were not discussed in this study broadly. The computed excess property values are presented in Table **2**, which also involves the values of K and molecular interaction parameters for all three systems. In Table **3**, theoretical values of ultrasonic velocity like Nomoto's relation, Junjie's relation, Impedance dependant relation, and Van Dael ideal mixing relation for all the ten concentrations (0.001 M -0.01M) and the corresponding % deviation, NI (ideal/non-ideal) and absolute average percentage deviation (AAPD) are given for all the three ternary systems along with corresponding experimental values of ultrasonic velocity. Table **4** illustrates the comparative study between the AAPD of theoretical values and chi-square test values. The experimental values of velocity, viscosity, and density are provided in Table **5**.

4.2. Role of Excess Adiabatic Compressibility

Fort and Moore found that the negative excess adiabatic compressibility values indicate that the greater interaction between the components of the mixture, whereas the positive excess values indicate the loosely packed molecules in the mixture due to their shape and size [35]. In the present investigation, it is observed that systems I and III, namely OMP+1-pentanol+n-hexane and MMP+1-pentanol+n-hexane, show the same tendency, i.e., both positive/negative values, respectively (Table **1**). But for system II, N, N-DMF+1-pentanol+n-hexane shows negative values. These values reveal that the negative results are due to associative types of interactions among the components, and positive/negative observations are because of both associative and dispersive types of interactions [36]. It is inferred that the systems I and III experienced a dispersive type of interaction due to the steric effect and inductive effect. System II possesses the associative type of interaction due to the absence of a steric effect. The plot between Conc. and Excess adiabatic compressibility for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K is represented in Figure **1**.

Table 2: Excess Properties / Thermodynamic Properties/ Experimental Studies for Systems I, II and III at 313 K

SI. No.	Name of the System	Property	Concentration X 10⁻³ (M)										Mean K value
			1	2	3	4	5	6	7	8	9	10	
1	OMP+1 PENTANOL+ nHEXANE	Experimental U ms⁻¹	1012.95	1013.96	1015.44	1013.20	1015.63	1013.61	1014.40	1013.51	1015.68	1014.68	
		Experimental η Nsm⁻² X10⁻⁴	5.196	5.198	5.278	5.16	5.204	5.3	5.228	5.141	5.299	5.228	
		Experimental ρ Kgm⁻³	788.2	788.7	789.9	788.7	789.3	788.7	787	785.3	789.9	787	
		Z^E Kg⁻²s⁻¹ X10⁺³	62.8	3.3	-51.3	-106.5	-151.7	-199.4	-242	-282.8	-313	-350	
		β^E Kg⁻¹ms² X10⁻¹⁰	-1.09	-0.81	-0.23	0.51	1.1	1.87	2.72	3.77	4.74	5.94	
		V_f^E (m³/mol) X10⁻⁸	0.238	0.238	0.233	0.24	0.238	0.231	0.236	0.242	0.232	0.236	
		L_f^E (A⁰)	-6.71	-6.44	-6.19	-5.94	-5.7	-5.48	-5.26	-5.05	-4.85	-4.66	
		π^E (Nm⁻²) X10⁺⁸	-0.18	-0.44	-0.71	-1.03	-1.27	-1.48	-1.73	-1.97	-2.1	-2.31	
		U^E ms⁻¹	-44.48	-66.37	-85.93	-107.56	-123.06	-141.71	-156.39	-171.70	-183.01	-196.63	
		Molecular interaction parameter X	-0.3240	-0.3227	-0.3207	-0.3237	-0.3205	-0.3232	-0.3222	-0.3234	-0.3205	-0.3218	
		K-value dm³ mol⁻¹	45.5	20.7	26.4	21.5	18.3	16.7	14.9	13.9	12.9	------	21.2
2	N,N-DMF+1-pentanol+nHEXANE	Experimental U ms⁻¹	1010.80	1011.14	1011.68	1012.28	1012.93	1013.17	1013.29	1013.43	1013.58	1013.66	
		Experimental η Nsm⁻² X10⁻⁴	5.03	5.04	5.06	5.1	5.15	5.18	5.19	5.21	5.26	5.32	
		Experimental ρ Kgm⁻³	798	798	798	798	798	798	799	799	799	799	
		Z^E Kg⁻²s⁻¹ X10⁺³	78.9	23.6	-27.4	-73.6	-117.4	-157.2	-194.1	-229.7	-262.9	-294.2	
		β^E Kg⁻¹ms² X10⁻¹⁰	-0.58	-1.18	-1.8	-2.44	-3.1	-3.78	-4.48	-5.21	-5.96	-6.74	

Top group

Parameter										
(top)										21.14
V_f^E (m³) X10⁻⁸	6.77	4.53	4.01	3.87	3.55	3.03	3.56	3.74	2.67	2.31
L_f^E (A⁰)	-6.7	-6.43	-6.18	-5.95	-5.74	-5.54	-5.35	-5.18	-5.01	-4.86
π^E (Nm⁻²) X10⁺⁸	0.047	0.014	0.093	0.074	0.048	0.024	0.003	-0.016	-0.034	-0.0396
U^E ms⁻¹	-44.892	-65.957	-85.155	-102.812	-119.101	-134.618	-149.193	-162.79	-175.51	-187.512
Molecular interaction parameter X	-0.3269	-0.3264	-0.3257	-0.3249	-0.3241	-0.3238	-0.3236	-0.3235	-0.3233	-0.3232
K-value dm³mol⁻¹	45.4	20.6	26.2	21.5	18.2	16.7	14.9	13.9	12.9	-----

3   MMP + 1 PENTANOL + nHEXANE

Parameter										
(top)										21.5
Experimental U ms⁻¹	1016.62	1017.12	1019.02	1022.83	1023.53	1026.94	1028.41	1030.71	1031.22	1033.61
Experimental η Nsm⁻² X10⁻⁴	5.88	6.012	6.101	6.141	6.165	6.154	6.221	6.28	6.29	6.314
Experimental ρ Kgm⁻³	856.1	857.2	858.4	858.2	859.2	860.1	860.2	860.3	860.2	861.2
Z^E Kg⁻²s⁻¹ X10⁺³	224.4	163.2	105.3	48.7	-6.8	-57.3	-107	-157.9	-208	-254.5
β^E Kg⁻¹ms² X10⁻¹⁰	-2.282	-1.679	-1.125	-0.512	0.268	1.026	1.974	2.927	4.102	5.424
V_f^E (m³) X10⁻⁸	-2.23	-1.07	-1.85	-1.77	-1.85	-2.04	-1.67	-1.6	-2.35	-2.39
L_f^E (A⁰)	-6.73	-6.45	-6.18	-5.91	-5.66	-5.42	-5.18	-4.95	-4.73	-4.52
π^E (Nm⁻²) X10⁺⁸	-3.33	-4.66	-5.26	-5.84	-6.41	-6.95	-7.47	-7.98	-8.47	-8.94
U^E ms⁻¹	-43.136	-68.973	-92.445	-113.095	-135.991	-155.359	-175.89	-194.853	-214.904	-232.409
Molecular interaction parameter X	-0.319	-0.318	-0.316	-0.311	-0.310	-0.305	-0.303	-0.300	-0.300	-0.296
K-value dm³mol⁻¹	45.8	20.9	26.5	21.9	18.5	17.1	15.3	14.3	13.2	-----

Table 3:   Theoretical Studies for Systems I, II and III at 313 K

Sl. No.	Name of the System	Values	1	2	3	4	5	6	7	8	9	10	AAPD
						Concentration X 10^{-3} (M)							
1	OMP+1 PENTANOL+ n-hexane	Nomoto's U(ms^{-1})	1049.18	1066.25	1083.65	1101.35	1119.39	1137.75	1156.45	1175.50	1194.90	1214.65	
		IMR U(ms^{-1})	1042.93	1054.66	1067.58	1081.70	1097.05	1113.66	1131.57	1150.85	1171.57	1193.83	
		Junj U(ms^{-1})	1033.92	1038.04	1044.93	1054.80	1067.98	1084.9	1106.16	1132.55	1165.21	1205.70	
		IMP U(ms^{-1})	1062.52	1088.60	1111.41	1131.52	1149.39	1165.38	1179.75	1192.76	1204.58	1215.36	
		Experimental(E) U(ms^{-1})	1012.95	1013.96	1015.44	1013.20	1015.63	1013.61	1014.40	1013.51	1015.68	1014.68	
		NI = U^2_{Exp}/U^2_{NOM}	0.9321	0.9043	0.8781	0.8463	0.8232	0.7937	0.7694	0.7434	0.7225	0.6978	
		NI = U^2_{Exp}/U^2_{IMR}	0.9433	0.9243	0.9047	0.8774	0.8571	0.8284	0.8036	0.7756	0.7516	0.7224	
		NI = U^2_{Exp}/U^2_{JUN}	0.9598	0.9541	0.9444	0.9227	0.9044	0.8729	0.841	0.8008	0.7598	0.7082	
		NI = U^2_{Exp}/U^2_{IMP}	0.9089	0.8676	0.8348	0.8018	0.7808	0.7565	0.7393	0.722	0.711	0.697	
		α	-0.0402	-0.0459	-0.0557	-0.0773	-0.0956	-0.1271	-0.159	-0.1992	-0.2402	-0.2918	
		% deviation (E-NOM)	-3.577	-5.157	-6.717	-8.699	-10.216	-12.247	-14.003	-15.983	-17.645	-19.708	-11.40
		% deviation (E-IMR)	-2.960	-4.014	-5.135	-6.760	-8.017	-9.871	-11.551	-13.551	-15.348	-17.656	-9.486
		% deviation (E-JUN)	-2.070	-2.375	-2.904	-4.105	-5.154	-7.033	-9.046	-11.745	-14.722	-18.826	-7.798
		% deviation (E-IMP)	-4.894	-7.361	-9.451	-11.677	-13.170	-14.973	-16.300	-17.686	-18.598	-19.778	-13.39
2	N,N-DMF+1-pentanol+n-hexane	Nomoto's U(ms^{-1})	1198.56	1200.26	1200.84	1201.13	1201.3	1201.42	1201.5	1201.56	1201.61	1201.65	
		IMR U(ms^{-1})	1052.04	1070.83	1088.81	1106.04	1122.57	1138.45	1153.7	1168.38	1182.51	1196.12	
		Junj U(ms^{-1})	1036.46	1036.46	1036.46	1036.46	1036.46	1036.46	1036.46	1036.46	1036.46	1036.46	
		IMP U(ms^{-1})	1063.69	1089.56	1111.3	1129.83	1145.82	1159.75	1171.99	1182.84	1192.51	1201.2	
		Experimental(E) U(ms^{-1})	1010.80	1011.14	1011.68	1012.28	1012.93	1013.17	1013.29	1013.43	1013.58	1013.66	
		NI = U^2_{Exp}/U^2_{NOM}	0.7112	0.7112	0.7112	0.7112	0.7112	0.7112	0.7112	0.7112	0.7112	0.7112	
		NI = U^2_{Exp}/U^2_{IMR}	0.9231	0.8916	0.8633	0.8376	0.8142	0.792	0.7714	0.7523	0.7347	0.7182	
		NI = U^2_{Exp}/U^2_{JUN}	0.9511	0.9407	0.9271	0.9098	0.8886	0.8626	0.8322	0.7974	0.7582	0.7142	

3 — MMP+1 PENTANOL+ nHEXANE

Parameter											
$NI = U^2_{Exp}/U^2_{IMP}$	0.903	0.8612	0.8288	0.8027	0.7815	0.7632	0.7475	0.7341	0.7224	0.7121	
α	-0.0489	-0.0593	-0.0729	-0.0902	-0.1114	-0.1374	-0.1678	-0.2026	-0.2418	-0.2858	
% deviation (E-NOM)	-18.575	-18.704	-18.698	-18.656	-18.597	-18.580	-18.574	-18.564	-18.551	-18.546	-18.60
% deviation (E-IMR)	-4.080	-5.903	-7.624	-9.262	-10.824	-12.365	-13.857	-15.290	-16.667	-18.000	-11.39
% deviation (E-JUN)	-2.539	-3.101	-3.857	-4.841	-6.083	-7.670	-9.620	-11.982	-14.843	-18.332	-8.287
% deviation (E-IMP)	-5.232	-7.756	-9.847	-11.612	-13.119	-14.467	-15.662	-16.716	-17.653	-18.501	-13.06
Nomoto's U (ms⁻¹)	1054.08	1054.08	1054.08	1054.08	1054.08	1054.08	1054.08	1054.08	1054.08	1054.08	
IMR U(ms⁻¹)	1045.34	1059.69	1075.48	1092.75	1111.55	1131.95	1154.05	1177.97	1203.86	1231.89	
Junj U(ms⁻¹)	1035.63	1041.75	1050.97	1063.59	1080.03	1100.88	1126.92	1159.27	1199.49	1249.87	
IMP U(ms⁻¹)	1072.41	1106.94	1137.06	1163.55	1187.03	1207.99	1226.82	1243.82	1259.24	1273.31	
Experimental(E) U(ms⁻¹)	1016.62	1017.12	1019.02	1022.83	1023.53	1026.94	1028.41	1030.71	1031.22	1033.61	
$NI = U^2_{Exp}/U^2_{NOM}$	0.9302	0.8935	0.8605	0.8318	0.7993	0.7721	0.7431	0.7164	0.6882	0.6636	
$NI = U^2_{Exp}/U^2_{IMR}$	0.9458	0.9213	0.8978	0.8761	0.8479	0.8231	0.7941	0.7656	0.7337	0.704	
$NI = U^2_{Exp}/U^2_{JUN}$	0.9636	0.9533	0.9401	0.9248	0.8981	0.8702	0.8328	0.7905	0.7391	0.6839	
$NI = U^2_{Exp}/U^2_{IMP}$	0.8987	0.8443	0.8032	0.7727	0.7435	0.7227	0.7027	0.6867	0.6706	0.6589	
α	-0.0363	-0.0467	-0.0599	-0.0752	-0.1019	-0.1298	-0.1672	-0.2095	-0.2609	-0.3161	
% deviation (E-NOM)	-3.68	-5.79	-7.80	-9.64	-11.85	-13.80	-16.00	-18.15	-20.54	-22.76	-13.00
% deviation (E-IMR)	-2.8	-4.2	-5.5	-6.8	-8.6	-10.2	-12.2	-14.3	-16.7	-19.2	-10.07
% deviation (E-JUN)	-1.87	-2.42	-3.14	-3.99	-5.52	-7.20	-9.58	-12.47	-16.32	-20.92	-8.343
% deviation (E-IMP)	-5.49	-8.83	-11.58	-13.76	-15.97	-17.63	-19.29	-20.68	-22.11	-23.19	-15.85

Table 4:   Comparative Study between Theoretical (AAPD) and Chi-Square Test Values for Systems I, II and III at 313 K

Sl. No.	System	AAPD				Mean Values of Chi-Square test			
		NOM	IMR	JUN	IMP	NOM	IMR	JUN	IMP
1	I	-11.395	-9.486	-7.798	-13.389	13.790	10.050	8.028	17.629
2	II	-18.604	-11.387	-8.287	-13.057	29.551	13.245	8.414	16.525
3	III	-13.003	-10.07	-8.343	-15.853	11.541	24.413	9.528	18.018

Table 5:   Experimental Values of Ultrasonic Velocity, Viscosity and Density of 1 Pentanol+n Hexane + OMP/NNDMF/MMP at 313 K

Sl. No.	CONC(M) $\times 10^{-3}$	Velocity (u) ms^{-1}			Viscosity (η) Nsm$^{-2}\times 10^{-4}$			Density (ρ) Kgm^{-3}		
		OMP	NNDMF	MMP	OMP	NNDMF	MMP	OMP	NNDMF	MMP
1	1	1012.95	1010.80	1016.62	5.196	5.03	5.880	788.2	798	856.1
2	2	1013.96	1011.14	1017.12	5.198	5.04	6.012	788.7	798	857.2
3	3	1015.44	1011.68	1019.02	5.278	5.06	6.101	789.9	798	858.4
4	4	1013.20	1012.28	1022.83	5.160	5.10	6.141	788.7	798	858.2
5	5	1015.63	1012.93	1023.53	5.204	5.15	6.165	789.3	798	859.2
6	6	1013.61	1013.17	1026.94	5.300	5.18	6.154	788.7	798	860.1
7	7	1014.40	1013.29	1028.41	5.228	5.19	6.221	787.0	799	860.2
8	8	1013.51	1013.43	1030.71	5.141	5.21	6.280	785.3	799	860.3
9	9	1015.68	1013.58	1031.22	5.299	5.26	6.290	789.9	799	860.2
10	10	1014.68	1013.66	1033.61	5.228	5.32	6.314	787.0	799	861.2

Figure 1: Plot between Conc. (M) X 10^{-3} and Excess adiabatic compressibility for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K.

4.3. Role of Excess Free Length

According to Fort, the positive values of excess free length is due to the dispersive forces, and the negative values are due to the charge transfer and hydrogen bond formation. In this present study, the negative values (Table **2**) of excess free length predicted the hydrogen bond and charge transfer complex formation in all three systems. This tendency is further supported by the positive values obtained for the β^E for systems I and III at higher concentrations which shows that breaking of a hydrogen bond is not possible in a 1-pentanol structure. The plot between Conc. and Excess free length for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K is presented in Figure **2**.
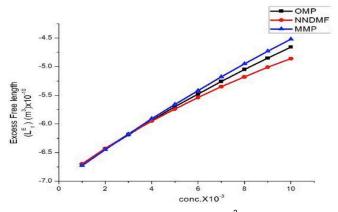

Figure 2: Plot between Conc. (M) X 10^{-3} and Excess free length for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K.

4.4. Role of Excess Free Volume

According to Sri Devi *et al*. [37], the negative values of the excess free volume are attributed to the stronger

molecular interactions. In this present probe, the positive values (Table **2**) are observed for the excess free volume of the system I and II, which pave the way for the inference of weak interactions. But for system III, the negative values are recorded, and hence molecular interactions are strong. The plot between Conc. and Excess free volume for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K is represented in Figure **3**.
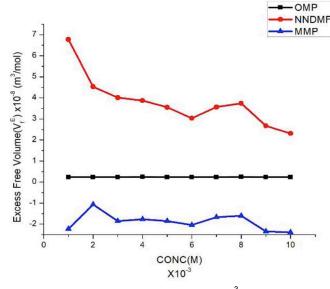

Figure 3: Plot between Conc. (M) X 10^{-3} and Excess free volume for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K.

4.5. Role of Excess Internal Pressure

The study of Internal pressure plays a vital role in deciding the thermodynamic properties of the liquid mixture. It is the measure of resultant forces of attraction and forces of repulsion between the component molecules in the liquid mixture and which may be due to donor-donor, donor-acceptor, or acceptor-acceptor forces of attractions. The positive values of excess internal pressure (Table **1**) show the weak interactions between the components of the liquid mixture, whereas the negative values account for the stronger interactions. In this present research, for systems I and III, the values are found to be negative, and hence strong interactions may be possible for the liquid mixtures, but for system II, the values are positive, thereby weak interaction, which is mainly due to the forces of repulsion between the component molecules. The plot between Conc. and Excess internal pressure for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K is represented in Figure **4**.

4.6. Role of Excess Acoustic Impedance

In the current study, the negative values (Table **1**) are got for the property called excess acoustic impedance, which indicates the weak interactions are
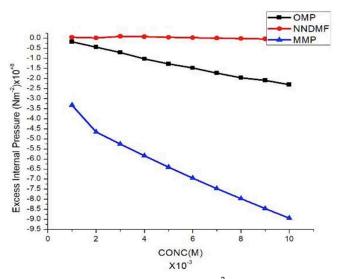

Figure 4: Plot between Conc. (M) X 10^{-3} and Excess internal pressure for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K.

possible for the II system. This is complemented by the results of Islam *et al*. [38]. For systems I and III, positive values are got at lower concentrations which paves the way for the presence of little stronger interactions is possible, and at the same time, negative values are obtained at higher concentrations that predict the weaker interactions, which is due to agitation of atoms among the components at an elevated working temperature of 313 K. The plot between Conc. and Excess acoustic impedance for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K is provided in Figure **5**.
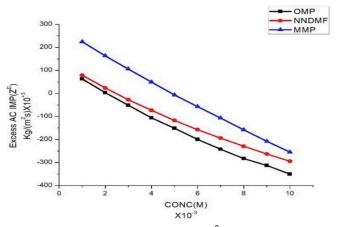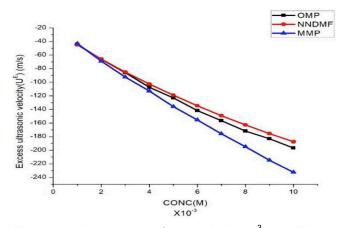

Figure 5: Plot between Conc. (M) X 10^{-3} and Excess acoustic impedance for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K.

4.7. Role of Excess Ultrasonic Velocity

In the present study, the values (Table **2**) of excess ultrasonic velocity are observed as negative irrespective of concentrations for systems I, II and III, which infer that weak interactions are possible in between the components in those systems. The negative values are got, which revealed weak

interaction are exhibited by all the systems due to thermal agitation, which is caused at 313 K. The corresponding plot is represented in Figure **6**. This statement is further supported by the values of K.

Figure 6: Plot between Conc. (M) X 10^{-3} and Excess ultrasonic velocity for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K.

4.8. Role of Molecular Interactions Parameter χ

The values (Table **3**) of molecular interaction parameter χ are found to be negative for the systems I, II, and III, which predict weaker interactions are possible among the components that may be attributed to the dissociation of intermolecular/intramolecular hydrogen bonding at higher concentrations at 313 K. This fact is supplemented by the adiabatic compressibility values.

4.9. Role of Stability Constant K

The properties such as polarizability, dipole moment, and dielectric constant of donor molecule decide the complex formation. The formation of constant K is the measure of molecular interaction of the components that come close together to form complexes. In the present study, to compare the stability of the charge transfer complex, the formation of constant K is calculated using the method of Kannappan [39]. These values are given in Table **1** for all three systems. It is observed that the K value is more or less the same for all three systems. This is due to the effect of dipole-dipole, dipole-induced dipole interaction, and inter/ intramolecular hydrogen bonding between the donor and acceptor in each and every system. It is noticed that the K value is comparatively higher for system III than the rest of the two systems, and hence the stability of the charge transfer complex is comparatively greater.

4.10. Theoretical Studies

Theoretical evaluations of ultrasonic velocity provided more reliable information about molecular arrangements in liquids. Several researchers carried out an ultrasonic investigation and correlated the dependant relation, and the results are interpreted in terms of molecular interactions [40]. The present investigation also, using theories such as IMR, IMP, JUN, and NOM relations to investigate the degree of molecular interaction in the ternary liquid mixtures. The deviation of the values of U^2_{Exp}/U^2_{IMX} from unity has been evaluated for explaining the non-ideality in the mixture.

From Table **3**, the theoretical values of ultrasonic velocity by the various theories show deviation from the experimental value. The observed deviation of ultrasonic velocity between theoretical value and experimental value shows that the molecular interaction takes place between the components in the liquid mixtures and indicates that considerable deviation from ideality because of dipole-dipole or dipole-induced dipole type of interaction [41]. The non-ideality of the system as a consequence of association or another type of interaction is called molecular interaction or degree of molecular interaction (α). The positive value of α shows the presence of strong interaction, and the negative value shows the presence of weak interaction [42]. In our present investigation, all the ternary liquid mixture exhibits negative values. This confirms the presence of weak interaction in all three ternary systems.
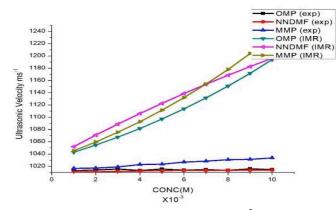
The theoretical studies determine the nature of molecular interactions in the liquid mixtures, which is under investigation [43]. The theoretical values of ultrasonic speed using the relations such as Van Dael Ideal Mixing Relation, Impedance Dependent Relation, Junjie's and Nomoto's relation, and the experimental ultrasonic velocities and the corresponding Absolute Average Percentage Deviation (AAPD) are calculated and tabulated in Table **3**. The order of theoretical relation concerning all the three systems based on their deviation is given below. The corresponding plots between Conc. and experimental and theoretical ultrasonic velocities (IMR/IMP/JUN/NOM) are given in Figures **7**, **8**, **9**, and **10**, respectively, for systems I, II, and III.

System I: $U_{IMP} > U_{NOM} > U_{IMR} > U_{JUN}$

System II: $U_{NOM} > U_{IMP} > U_{IMR} > U_{JUN}$

System III: $U_{IMP} > U_{NOM} > U_{IMR} > U_{JUN}$

It is observed from Table **3** that the AAPD values of Junjie's relation for all the systems are in good agreement with experimental values, i.e., the least percentage of deviation when compared with the rest of the two systems among all the four relations which are considered for the study.

Figure 7: Plot between Conc. (M) X 10^{-3} and ultrasonic velocity of experimental and ideal mixing relation theory for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K.
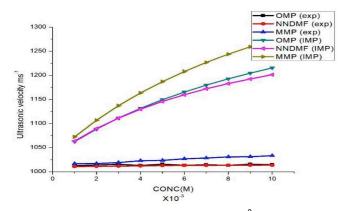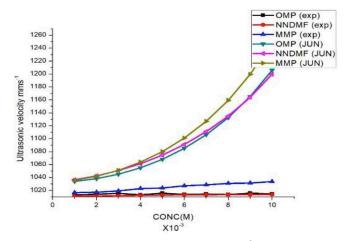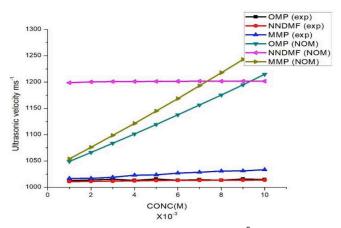

Figure 8: Plot between Conc. (M) X 10^{-3} and ultrasonic velocity of experimental and impedance dependent relation theory for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K.

Figure 9: Plot between Conc. (M) X 10^{-3} and ultrasonic velocity of experimental and Junjie's relation for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K.

From Table **3**, it is observed that the values of NI according to which if there is a gradual increase/decrease in value implies linearity of the system whereas uneven increase/decrease in values predict the non-linearity of the system. In the present study, for all the three systems with respect to all the theoretical relations, the values are found to be

decreased gradually. Hence the systems I, II, and III (OMP/N, N-DMF/MMP+1-pentanol+n-hexane) are believed to be linear.

Figure 10: Plot between Conc. (M) X 10^{-3} and ultrasonic velocity of experimental and Nomoto's theory for OMP/ N, N-DMF/MMP+1-pentanol+n-hexane at 313 K.

4.11. Statistical Analysis

Finally, the Chi-square goodness of fit determines or confirms the overall validity of one of the theories. From Table **4**, it is noted that the theoretical values of ultrasonic velocity revealed that there is a greater deviation for all the systems I, II, and III for all the theories except Junjie's relation, which are considered when compared with that of Chi-square goodness of fit test. Only Junjie's relation showed the very least deviation calculated with respect to Chi-square analysis. Both the theoretical values obtained by using Junjie's relation and the chi-square analysis values are found to be in good agreement, which confirms the experimental study and according to which a weak interaction is predicted due to polarizability, dipole-dipole, dipole-induced dipole, intra/intermolecular hydrogen bonding exhibited by each and every component of all the systems [44].

5. CONCLUSION

From the magnitude and variations of acoustic and excess properties, the present study reveals the existence of molecular interactions, which may be caused due to various parameters like dipole-dipole, dipole-induced dipole interactions, hydrogen bond, and charge transfer complex formation. Among the three systems I, II, and III, which are under probe, it is concluded that a charge transfer complex has been formed for all three systems, which may be attributed to their more or less same K value. It is also concluded from the values of excess properties like adiabatic compressibility, free length, free volume, internal pressure, ultrasonic velocity, and acoustic impedance that weak interactions are exhibited for all three systems. It is also concluded from the values of excess

properties, particularly Internal Pressure, Free volume, and K, that comparatively strong interactions are possible for system III. With respect to theoretical studies, among the four theories like IMR, IMP, JUN, and NOM relations which are considered for the present study, Junjie's relation yielded an excellent comparable result with that of experimental ultrasonic velocities. Besides, it is concluded that Chi-square goodness of fit is best suited for Junjie's relation for all three systems.

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