Publications

Available Online

J. Sci. Res. **14** (3), 917-929 (2022)

JOURNAL OF SCIENTIFIC RESEARCH

www.banglajol.info/index.php/JSR

Comparative Study of Molecular Interaction in Ternary Liquid Mixtures of Polar and Non-Polar Solvents

B. Samantaray[1, 3*], **M. K. Praharaj**[2], **B. R. Das**[3], **S. P. Das**[1]

[1]Department of Chemistry, Ravenshaw University, Cuttack, Odisha, India

[2]Deaprtment of Physics, Ajay Binay Institute of Technology, Cuttack, Odisha, India

[3]Department of Chemistry, Odisha University of Technology and Research, Odisha, India

Received 12 January 2022, accepted in final revised form 26 May 2022

Abstract

Ultrasonic velocity measurements, density measurements, and viscometric studies were conducted for the ternary mixture of pyridine and toluene separately with N, N-dimethylformamide (DMF) in butanol, at different temperatures and for different concentrations of component liquids. Using these basic experimental data, various acoustic and thermodynamic parameters, such as adiabatic compressibility (β), free length ($L_{f,}$), free volume (V_f), etc. were calculated. Also, Excess thermo-acoustical parameters were calculated from the experimentally measured data. The outcomes were expressed in terms of the molecular interactions and the variations in parameters under varying solute concentrations. A comparative study is discussed. Variation in the above parameters for the different mixtures is indicative of the nature of the interactions between the components in the liquid mixture. Concluding remarks regarding intermolecular interactions are provided.

Keywords: Ternary mixture; Ultrasonic velocity; Adiabatic compressibility; Free length.

doi: http://dx.doi.org/10.3329/jsr.v14i3.57587 J. Sci. Res. **14** (3), 917-929 (2022)

1. Introduction

The measurement of density, viscosity, and ultrasonic velocity of liquid mixtures consisting of polar and non-polar components is important in understanding the intermolecular interaction between the component molecules and finding applications in several industrial and technological processes [1-8]. This has been studied for various binary and ternary mixtures [9,10] concerning variation in concentration and temperature. The ultrasonic techniques [11-16] are used frequently because of their ability to characterize the Physio-chemical behavior of the liquid system. The measurement of ultrasonic velocity in liquid mixtures and some excess parameters reveals the degree of deviation from ideality whenever there are interactions among the component molecules.

N, N-Dimethylformamide (C_3H_7NO) DMF is a polar non-aqueous solvent with dipole-dipole interaction between the molecules in a pure state. Therefore, it acts as an

---

[*] *Corresponding author*: m_praharaj@rediffmail.com

aprotic, photophilic medium with a dipole moment (3.9 D) and a high dielectric constant (36.7). Pyridine (C_5H_5N) is a polar aprotic solvent. It is used in various reactions, including electrophilic substitution, nucleophilic substitution, oxidation, and reduction, as it has the property of forming complexes with many salts. It has a dipole moment of 2.2 D at 298 K and a dielectric constant (12.3), which is small compared to DMF. n-Butanol is a primary alcohol with the chemical formula C_4H_9OH and a linear structure. Butanol is used as a raw material for coating resins; on the other hand, it is widely used as a solvent because many organic materials are soluble in it. Toluene is a polar aprotic solvent due to the presence of an electron releasing methyl group. The Methyl group of toluene is an electron donor group through induction. It enhances the 'π' electron density in the toluene ring.

In the present work, various acoustic and related thermodynamic parameters are studied to investigate the interactions between the components of two ternary liquid mixtures containing pyridine and toluene with DMF and butanol. Also, a comparative statement is given for these two ternary mixture.

2. Experimental

The ternary solvent mixtures of various concentrations in mole fraction were prepared by taking analytical reagent grade and spectroscopic reagent grade chemicals with a minimum assay of 99.9 % and obtained from E-Merck Ltd (India). All the component liquids were purified by the standard methods [17]. In all the mixtures, the mole fraction of the second component, butanol ($X_2 = 0.46$), was kept fixed while the mole fractions of the remaining two (X_1(DMF) and X3pyridine or toluene) were varied from 0.0 to 0.6, to have the mixture of different concentration. There is nothing significant in fixing the mole fraction of the second component at 0.46. The density, viscosity, and ultrasonic velocity were measured as a function of the concentration of the ternary liquid mixture at different temperatures. Ultrasonic velocity measurements were made using an ultrasonic interferometer (Model M-84, supplied by M/S Mittal Enterprises, New Delhi) at 2 MHz with an accuracy of $\pm 0.1\ \mathrm{m \cdot s^{-1}}$. The measuring cell of an interferometer is a specially designed double-walled vessel with provision for temperature constancy. An electronically operated digital constant temperature bath (Model SSI-03 Spl, supplied by M/S Mittal Enterprises, New Delhi), operating in the temperature range of −10 °C to 85 °C with an accuracy of ±0.1 °C has been used to circulate water through the outer jacket of the double-walled measuring cell containing the experimental liquid. The viscosity of all the solutions was measured by LOVIS-2000 M/ME of Anton Parr, making it suited for low viscosity liquids at different temperatures, which work on the rolling ball principle. The density of all the solutions was measured by Anton-Parr DSA5000M Density meter having an oscillating U- tube. The temperature of the U-tube was maintained by an inbuilt Peltier thermostat.

3. Theoretical Aspects

The following thermodynamic parameters were calculated from measured density, viscosity, and ultrasonic velocity values.

(i) Adiabatic compressibility (β): Adiabatic compressibility is the fractional decrease of volume per unit increase of pressure when no heat flows in to or out of the system. It is calculated from the ultrasonic velocity (U) in $ms^{-1}$and the density (ρ) in $Kgm^{-3}$of the medium by using the equation of Newton Laplace [18] as,

$$\beta = 1/U^2.\rho \tag{1}$$

(ii) Intermolecular free length (L_f): The intermolecular free length is the distance between the surfaces of the neighboring molecules. It is calculated by using the relation [19],

$$L_f = K_T\beta^{1/2} \tag{2}$$

Where 'K_T'' is the temperature-dependent constant called Jacobson's constant{(93.875+0.375T) X10^{-8}} [20] T is the absolute temperature and 'β' is the adiabatic compressibility.

(iii) Free volume (V_f): Free volume is one of the significant factors in explaining the variations in the physio-chemical properties of liquids and liquid mixtures, which depends on the shape, size, and structural arrangements of molecules in the mixture. [21] Free volume can be calculated by using the measured values of ultrasonic velocity (U) and the viscosity (η) of liquid [22] as follows

$$V_f = (M_{eff}.U/K.\eta)^{3/2} \tag{3}$$

Where 'M_{eff}' is the effective mlecular weight, ($M_{eff} = \sum_{i=1}^{n} M_i X_i$ in which Mi and Xi are the molecular weight and the mole fraction of the individual constituents, respectively), 'K' is a dimensionless constant independent of temperature and liquid. Its value is 4.281 × 10^9 [23].

(iv) Internal pressure (π_i): The measurement of internal pressure is important in the study of the thermodynamic properties of liquids. The internal pressure is the cohesive force, which is a result of the force of attraction and force of repulsion between the molecules. It is calculated by using the relation [24],

$$\pi_i = bRT\ (K\eta/U)^{1/2}\ (\rho^{2/3}/M^{7/6}) \tag{4}$$

Where, 'b' stands for cubic packing, which is assumed to be '2' for all liquids, 'R' is the Universal gas constant, 'η' is the viscosity of solution in $N.S.m^{-2}$.

(v) Relaxation time (τ): Relaxation time is the time taken for the excitation energy to appear as translational energy, and it depends on temperature and impurities. The relaxation time can be calculated from the relation,

$$\tau = 4/3.\ (\beta.\eta) \tag{5}$$

(vi) Acoustic impedance (Z): Acoustic impedance is a measure of the ease with which a sound wave propagates through a particular medium and relates to the elastic properties of the medium [25,26]. The acoustic impedance is given by,

$$Z = U.\rho \tag{6}$$

(vii) Gibb's free energy: The change in Gibb's free energy is calculated by using the relation

$$\Delta G = kT.\ln (kT\tau/h) \tag{7}$$

'k' is Boltzmann's constant and 'h' is Planck's constant.

(viii) Available volume: Available volume is the direct measure of compactness and strength of binding between liquid or liquid mixture molecules. Schaff *et al.* [21,27] showed that the available volume could be obtained by the relation.

$$V_a = Vm(1\text{-}U/Um) \tag{8}$$

U_m= the Schaaf's limiting value taken as 1600 m/s for liquid mixture
U= Ultrasonic velocity of the mixture

(ix) Excess parameters (A^E): In order to study the non-ideality of the liquid mixtures, the difference between the values of the real mixture (Aexp) and those corresponding to an ideal mixture (Aid), namely the excess parameters (A^E) of some of the acoustic parameters, were computed using the equation **[**28]

$$A^E = A_{exp} - A_{id} \tag{9}$$

Where $A_{id} = \sum_{i=1}^{n} A_i X_i$ 'A_i' is any parameter and 'X_i' the mole fraction of 'i'th component in the liquid mixture.

3. Results and Discussion

The measured density, viscosity, and ultrasonic velocity of two types of the ternary mixture, S1 (DMF-butanol-pyridine) and S2 (DMF-butanol-toluene), are represented in Table 1. These three measured parameters decrease with an increase in temperature for a fixed mole fraction of pyridine or toluene. They are found to have a higher value of DMF-butanol-pyridine mixture than DMF-butanol-toluene (Fig. 1).

Thermal agitation increases the vibration of molecules reducing the intermolecular forces of attraction. Hence the molecules move apart, increasing the internal space with an increase in temperature. More intermolecular space leads to an increase in the volume of the solution and a decrease in the density (Fig. 1a). The self-association of a molecule in its pure state is either Vander walls interaction, dipole-dipole interaction, a hydrogen bond, or a mixture of all the above types. The interaction of DMF and butanol is either an intermolecular hydrogen bond or dipole-dipole interaction. When pyridine or toluene is introduced/added to the system, it affects the existing intermolecular force. The higher density value for pyridine indicates larger interaction in DMF-butanol-pyridine than DMF-butanol-yoluene. (Fig. 1d).

Table 1. Experimental values of density, viscosity, and ultrasonic velocity at different temperatures.

Mole fraction		Density (Kg/m^3)				Viscosity(η) NSm^{-2} (x 10^{-3})				Ultrasonic Velocity (ms^{-1})			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K	288K	298K	308K	318K
S1: DMF - Butanol – Pyridine													
0.12	0.42	0.9021	0.8930	0.8838	0.8741	1.0693	0.9131	0.7939	0.6935	1370.4	1334.4	1324.9	1313.2
0.21	0.33	0.8975	0.8885	0.8794	0.8701	1.0834	0.9272	0.8024	0.7018	1336.1	1328.2	1321.6	1318.2
0.29	0.25	0.8935	0.8844	0.8753	0.8662	1.0631	0.9168	0.7933	0.6995	1328.3	1323.1	1320.5	1304.5
0.38	0.16	0.8929	0.8839	0.8748	0.8656	1.0425	0.9005	0.7829	0.6869	1319.8	1308.1	1294.8	1284.1
0.47	0.07	0.8883	0.8794	0.8703	0.8611	1.0453	0.8996	0.7824	0.6875	1310.8	1297.8	1281.4	1272.9
0.54	0.00	0.8852	0.8763	0.8673	0.8582	1.0385	0.8965	0.7800	0.6877	1288.0	1264.8	1251.3	1233.2
S2: DMF -Butanol – Toluene													
0.09	0.45	0.8483	0.8394	0.8303	0.8210	0.8790	0.7510	0.6518	0.5705	1336.4	1323.0	1299.6	1283.7
0.19	0.35	0.8564	0.8476	0.8385	0.8293	0.9106	0.7822	0.6796	0.6016	1369.8	1327.5	1301.8	1273.7
0.28	0.26	0.8632	0.8543	0.8452	0.8362	0.9264	0.8063	0.7003	0.6185	1338.9	1322.1	1301.5	1287.7
0.37	0.17	0.8686	0.8598	0.8508	0.8417	0.9725	0.8365	0.7278	0.6413	1308.6	1294.2	1257.7	1234.6
0.46	0.08	0.8787	0.8698	0.8608	0.8517	1.0305	0.8868	0.7680	0.6776	1293.6	1281.8	1253.1	1222.8
0.54	0.00	0.8852	0.8763	0.8673	0.8582	1.0385	0.8965	0.7800	0.6877	1288.0	1264.8	1251.3	1233.2

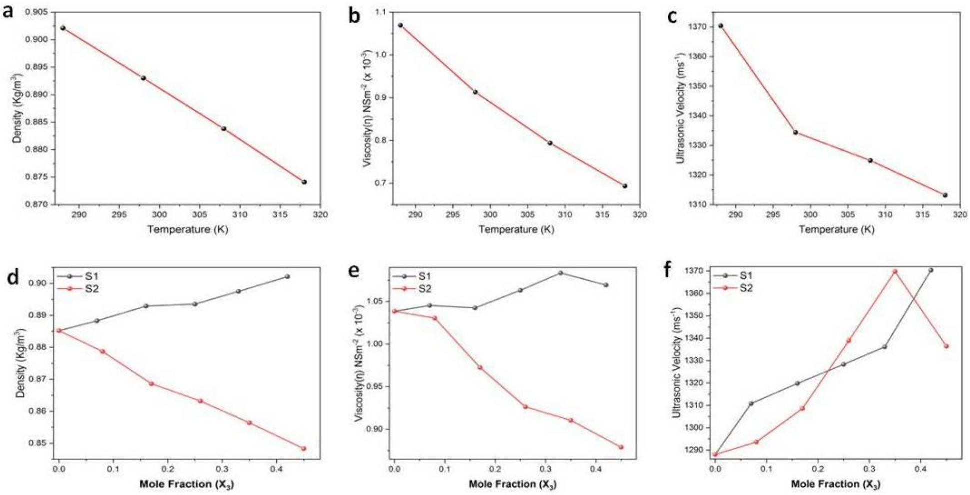
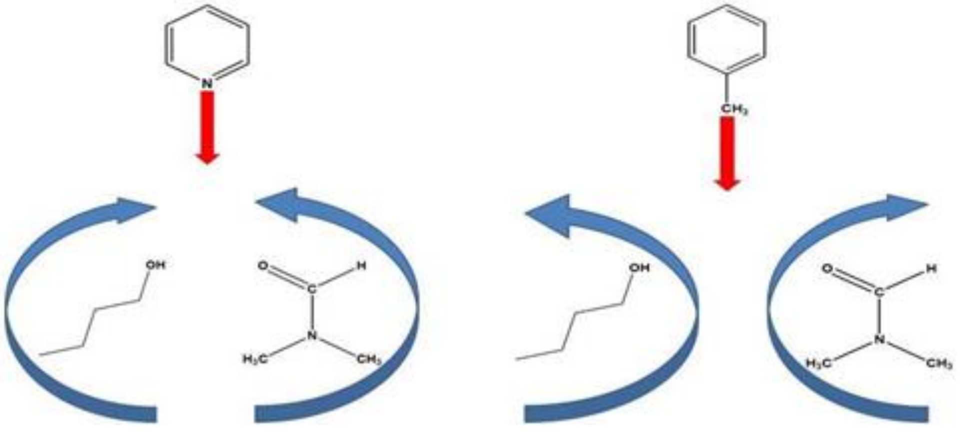


Fig. 1. Variation of density(a), viscosity(b) and ultrasonic velocity (c) with temperature. Compared value of density (d), viscosity (e), and ultrasonic velocity (f) with mole fraction of third component (X3) between DMF-Butanol-Pyridine and DMF-Butanol-Toluene system at a constant temperature.

At constant temperature, density and viscosity increase with the increase in mole fraction of pyridine but decrease with the increase in mole fraction of toluene. The association of molecules in DMF is dipole-dipole type; in butanol, it is an intermolecular hydrogen bond type, while in the mixture of DMF-butanol, it is also an intermolecular hydrogen bond. With the addition of pyridine, the interaction between pyridine and butanol increases due to the presence of a strong intermolecular hydrogen bond between them which increases with the increase in the mole fraction of pyridine. The lower value of density for a system containing toluene than pyridine is due to the non-polar nature of toluene. The non-polar toluene molecules move DMF and butanol away from each other and reduce the interaction between DMF and butanol as in Scheme 1. When more and more toluene is added to a binary mixture of DMF and butanol, the existing attractive interaction reduces the density and viscosity decrease.

Table 2. Calculated values of adiabatic compressibility relaxation time and free length at different temperatures.

Mole fraction		Adia. Compressibility x 10^{-10}				Relaxation time (x 10^{-12})				Free length (x 10^{-10})			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K	288K	298K	308K	318K
S-1: DMF + Butanol + Pyridine													
0.12	0.42	5.903	6.289	6.446	6.634	0.842	0.766	0.682	0.613	0.476	0.497	0.513	0.523
0.21	0.33	6.241	6.380	6.510	6.614	0.902	0.789	0.697	0.619	0.490	0.500	0.516	0.522
0.29	0.25	6.343	6.459	6.552	6.784	0.899	0.790	0.693	0.633	0.494	0.503	0.517	0.529
0.38	0.16	6.430	6.612	6.818	7.006	0.894	0.794	0.712	0.642	0.497	0.509	0.528	0.538
0.47	0.07	6.552	6.751	6.998	7.167	0.913	0.810	0.730	0.657	0.502	0.515	0.535	0.544
0.54	0.00	6.805	7.128	7.358	7.657	0.942	0.852	0.765	0.702	0.511	0.529	0.548	0.562
S2: DMF -Butanol – Toluene													
0.09	0.45	6.601	6.807	7.131	7.392	0.774	0.682	0.620	0.562	0.504	0.517	0.540	0.552
0.19	0.35	6.223	6.695	7.037	7.433	0.756	0.698	0.638	0.596	0.489	0.512	0.536	0.554
0.28	0.26	6.463	6.697	6.984	7.212	0.798	0.720	0.652	0.595	0.498	0.512	0.534	0.545
0.37	0.17	6.723	6.944	7.431	7.794	0.872	0.774	0.721	0.666	0.508	0.522	0.551	0.567
0.46	0.08	6.800	6.997	7.398	7.852	0.934	0.827	0.758	0.709	0.511	0.524	0.550	0.569
0.54	0.00	6.805	7.128	7.358	7.657	0.942	0.852	0.765	0.702	0.511	0.529	0.548	0.562



Scheme 1. Synergistic effects by which butanol and DMF approach each other with the approach of pyridine and moving away of butanol and DMF with the approach of toluene.

The ultrasonic velocity increases with an increase in mole fraction of toluene or pyridine can be explained based on the arrangement of molecules in bulk. The velocity increases with the increase in mole fraction of both pyridine and toluene, which implies both the system is well arranged for the propagation of sound waves at higher concentrations. However, a higher velocity value for pyridine than toluene indicates the ternary solution containing pyridine is more organized in pyridine than containing toluene.

Table 3. Calculated acoustic impedance values, Gibb's free energy, and internal pressure at different temperatures.

Mole fraction		Acoustic Impedance (x 10^6)				Gibb's free energy (x 10^{-20})				Internal Pressure x 10^6			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K	288K	298K	308K	318K
S-1: DMF + Butanol + Pyridine													
0.12	0.42	1.236	1.192	1.171	1.148	1.163	1.201	1.238	1.275	1.882	1.812	1.740	1.674
0.21	0.33	1.199	1.180	1.162	1.147	1.166	1.202	1.239	1.275	1.912	1.824	1.746	1.676
0.29	0.25	1.187	1.170	1.156	1.130	1.166	1.202	1.238	1.276	1.894	1.811	1.731	1.677
0.38	0.16	1.178	1.156	1.133	1.112	1.165	1.202	1.240	1.277	1.881	1.805	1.736	1.674
0.47	0.07	1.164	1.141	1.115	1.096	1.166	1.203	1.241	1.278	1.883	1.805	1.739	1.676
0.54	0.00	1.141	1.109	1.086	1.059	1.168	1.205	1.243	1.281	1.831	1.764	1.698	1.647
S2: DMF -Butanol – Toluene													
0.09	0.45	1.134	1.110	1.079	1.054	1.160	1.196	1.234	1.271	1.606	1.533	1.479	1.426
0.19	0.35	1.173	1.125	1.092	1.056	1.159	1.197	1.235	1.273	1.625	1.572	1.519	1.481
0.28	0.26	1.156	1.129	1.100	1.077	1.161	1.198	1.236	1.273	1.667	1.608	1.550	1.501
0.37	0.17	1.137	1.113	1.070	1.039	1.164	1.201	1.240	1.278	1.735	1.663	1.615	1.568
0.46	0.08	1.137	1.115	1.079	1.041	1.167	1.204	1.242	1.281	1.810	1.733	1.675	1.632
0.54	0.00	1.141	1.109	1.086	1.059	1.168	1.205	1.243	1.281	1.831	1.764	1.698	1.647

The excess viscosity is one of the important parameters to indicate the strength of molecular interaction in a mixture. The value of excess viscosity shown in Table 5 is negative for both the ternary systems and decreases with an increase in the mole fraction of pyridine and toluene (Fig. 4b). According to Fort and Moore, a positive excess viscosity value is due to the existence of shorter specific interactions like the formation of a complex in the liquid mixture, while a negative excess viscosity value is due to dispersion, induction, and dipolar force between the molecule [29]. In our system, negative value advocates the existence of weak dipole force in the liquid mixture. The higher negative excess viscosity for toluene than pyridine suggests more decrease in interaction in DMF-butanol -toluene than DMF-butanol-pyridine due to the lower value of dipole moments of toluene than pyridine.

Table 4. Calculated values of free volume, available volume, and molar volume at different temperatures.

Mole fraction		Free volume x 10^{-7}				Available volume				Molar Volume			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K	288K	298K	308K	318K
S-1: DMF + Butanol + Pyridine													
0.12	0.42	4.032	9.748	12.521	15.901	29.00	33.89	35.47	37.39	202.1	204.2	206.3	208.6
0.21	0.33	3.806	9.460	12.276	15.709	33.51	34.86	36.07	36.91	203.1	205.2	207.3	209.5
0.29	0.25	3.882	9.566	12.473	15.541	34.65	35.68	36.39	38.87	204.1	206.2	208.3	210.5
0.38	0.16	3.959	9.661	12.352	15.598	35.76	37.63	39.75	41.59	204.2	206.3	208.4	210.6
0.47	0.07	3.903	9.561	12.173	15.374	37.10	39.16	41.71	43.29	205.2	207.3	209.5	211.7
0.54	0.00	4.000	9.247	11.801	14.654	41.25	44.77	47.06	50.03	211.5	213.7	215.9	218.2
S2: DMF -Butanol – Toluene													
0.09	0.45	5.429	12.902	16.351	20.598	36.40	38.65	42.38	45.13	220.9	223.3	225.7	228.3
0.19	0.35	5.344	12.200	15.397	18.800	31.48	37.66	41.65	46.08	218.8	221.1	223.5	226.0

0.28	0.26	5.032	11.586	14.715	18.332	35.43	38.10	41.36	43.74	217.1	219.4	221.7	224.1
0.37	0.17	4.521	10.619	13.193	16.301	39.29	41.66	47.12	50.85	215.7	218.0	220.3	222.6
0.46	0.08	4.073	9.589	12.104	14.794	40.84	42.85	47.20	51.87	213.3	215.5	217.7	220.0
0.54	0.00	4.000	9.247	11.801	14.654	41.25	44.77	47.06	50.03	211.5	213.7	215.9	218.2

The variation of adiabatic compressibility and intermolecular free length with the variation of temperature and mole fraction of pyridine or toluene are shown in Table 2 and Fig. 2. These values decrease with an increase in mole fraction of pyridine or toluene and temperature; the higher values are observed for toluene than pyridine. The higher value of adiabatic compressibility and free length of the toluene system than in the pyridine system explains that the intermolecular space is more in the toluene system than in pyridine. This confirms the intermolecular force of attraction in DMF-butanol-pyridine is more than that DMF-butanol -toluene, i.e., the former is more associated than the latter. The excess value of adiabatic compressibility, free length, and free volume are shown in Table 6. The positive value of excess adiabatic compressibility, excess free length, and excess free volume for both systems indicates the existence of weak interaction between the components in the system and at the same time at a particular concentration. The free length and adiabatic compressibility increase with temperature, which supports the existence of weak interaction between molecules. Both excess parameters are found more for the toluene system than the pyridine system, which suggests the intermolecular distance between DMF-butanol-toluene is more than DMF-butanol-pyridine confirms that the interaction in the toluene system is less than pyridine system. In both cases, a drastic change in properties was observed between 0.3 to 0.4 mole fraction, indicating specific molecular interaction /structure breaking at a higher mole fraction.

Table 5. Excess values of density, viscosity, and ultrasonic velocity at different temperatures.

Mole fraction		Excess Density (Kg/m^3)				Excess Viscosity(η) NSm^{-2} ($x10^{-3}$)				Excess Velocity (ms^{-1})			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K	288K	298K	308K	318K
S-1: DMF + Butanol + Pyridine													
0.12	0.42	-0.020	-0.021	-0.023	-0.024	-0.482	-0.539	-0.438	-0.373	-173.60	-120.7	-37.74	16.94
0.21	0.33	-0.019	-0.018	-0.019	-0.020	-0.522	-0.531	-0.429	-0.354	-89.18	150.82	-42.28	18.45
0.29	0.25	-0.019	-0.020	-0.020	-0.021	-0.601	-0.587	-0.463	-0.374	230.79	2.33	-47.14	46.04
0.38	0.16	-0.024	-0.023	-0.023	-0.024	-0.666	-0.690	-0.536	-0.411	-1.39	35.28	-45.14	-55.61
0.47	0.07	-0.231	-0.223	-0.213	-0.214	-0.541	-0.604	-0.474	-0.373	-178.17	-88.77	65.12	52.70
0.54	0.00	-0.787	-0.565	-0.391	-0.394	-0.701	-0.61	-0.463	-0.351	-109.01	-97.35	-88.47	-74.74
S2: DMF -Butanol – Toluene													
0.09	0.45	0.089	0.046	-0.037	-0.103	-0.682	-0.616	-0.4637	-0.347	21.82	46.96	59.26	82.78
0.19	0.35	-0.006	0.008	-0.021	-0.066	-0.687	-0.613	-0.4621	-0.340	41.19	35.93	45.96	57.25
0.28	0.26	-0.268	-0.207	-0.184	-0.200	-0.708	-0.617	-0.4678	-0.348	-4.16	14.62	29.80	55.35
0.37	0.17	-0.672	-0.549	-0.473	-0.483	-0.699	-0.615	-0.4669	-0.350	-49.10	-29.40	-30.07	-13.81
0.46	0.08	-0.571	-0.407	-0.283	-0.284	-0.677	-0.593	-0.4530	-0.338	-78.13	-57.27	-50.17	-41.14
0.54	0.00	-0.787	-0.565	-0.391	-0.394	-0.701	-0.605	-0.4632	-0.351	-109.01	-97.35	-88.47	-74.74

The variation of Gibbs free energy and its excess value with the mole fraction and temperature are shown in Tables 3 and 7.

The excess free energy of both systems is negative in all temperature ranges. It decreases with increasing mole fraction of pyridine and toluene at a constant temperature. The minimum value for pyridine is between 0.2 -0.3 mole fractions, while the value for toluene is 0.3-0.4. The excess free energy of the toluene system is more than the pyridine system. According to Reed et al., the positive value of excess free energy may be due to specific interactions like hydrogen bond and charge transfer, while a negative value is due to the prominence of dispersion forces [28]. The increase in the trend of the negative value of free energy suggests a decrease in interaction between molecules with the addition of toluene. When toluene is added to the DMF-butanol system, the initial intermolecular hydrogen bond between DMF-butanol gets broken, weakening the interactions. It is also observed that when the mole fraction of both the system crosses the magical point of 0.3, a drastic variation in properties occurs

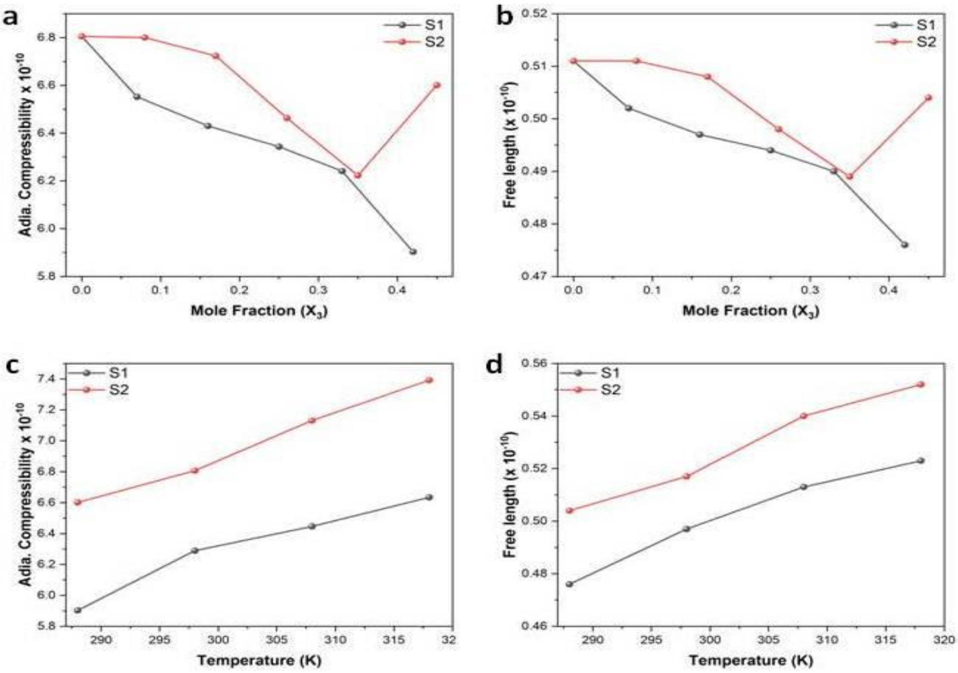


Fig. 2. Variation of (a) Adiabatic compressibility (b) free length with mole fraction of the third component (X_3) and (c) adiabatic compressibility (d) free length with temperature for both systems S1and S2 system.

Table 6. Excess values of adiabatic impedance relaxation time and free length at different temperatures.

Mole fraction		Excess Adia. Compressibility x 10^{-10}				Excess Free volume x 10^{-7}				Excess Free length (x 10^{-10})			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K	288K	298K	308K	318K
S-1: DMF + Butanol + Pyridine													

0.12	0.42	1.51	0.97	0.17	0.38	1.245	1.917	2.804	3.815	1.991	1.361	0.383	0.294
0.21	0.33	0.63	1.28	0.22	0.40	1.610	2.971	2.918	3.942	0.930	1.587	0.431	0.326
0.29	0.25	1.62	0.19	0.29	0.65	2.942	2.847	3.312	4.607	2.135	0.096	0.517	0.644
0.38	0.16	0.10	0.43	0.31	0.46	2.566	3.861	4.173	4.689	0.004	0.418	0.528	0.706
0.47	0.07	1.69	0.74	0.71	0.67	1.702	3.007	4.633	5.452	2.156	1.037	0.778	0.692
0.54	0.00	8.94	8.18	7.90	6.87	2.565	3.793	4.919	5.883	1.190	1.088	1.048	0.913
S2: DMF -Butanol – Toluene													
0.09	0.45	-2.63	-5.44	-7.21	-10.75	3.395	4.577	5.686	7.046	-0.298	-0.63	-0.831	-1.213
0.19	0.35	-4.72	-4.63	-6.07	-8.06	3.503	4.398	5.425	6.428	-0.537	-0.51	-0.677	-0.882
0.28	0.26	-0.66	-2.71	-4.54	-8.01	3.384	4.265	5.298	6.441	-0.023	-0.26	-0.480	-0.866
0.37	0.17	3.60	1.67	1.98	0.07	3.066	3.947	4.753	5.711	0.509	0.277	0.311	0.093
0.46	0.08	6.06	4.13	3.74	2.93	2.813	3.597	4.424	5.232	0.825	0.591	0.540	0.443
0.54	0.00	8.94	8.18	7.90	6.87	2.565	3.793	4.919	5.883	1.190	1.088	1.048	0.913

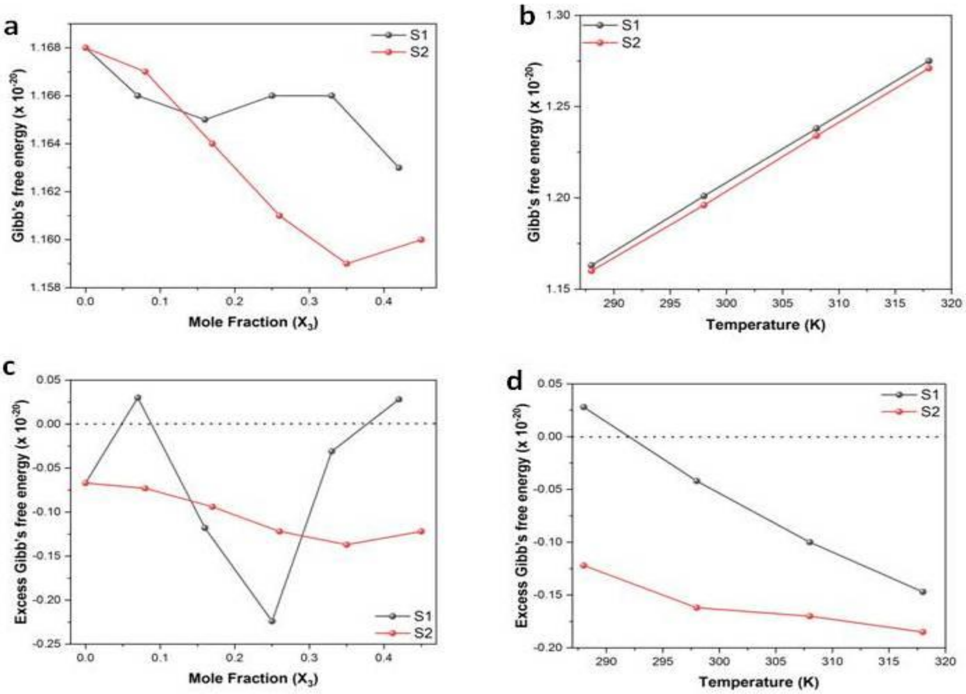


Fig. 3. Variation of Gibbs Free energy and excess Gibbs Free energy of both S1 and S2 system with mole fraction (a, c) of the third component(X3) and (b, d) with temperature.

The decrease in excess value of excess Gibbs free energy in the pyridine system with an increase in concentration indicates the weakening of interaction between solvent molecules is more pronounced in toluene than in pyridine. This may be due to the lower dipole moment of toluene. But throughout the study, the effects of change in mole fraction in the tcase of pyridine are much more prominent than that of toluene may be due to a higher degree of polarity in pyridine due to the presence of lone pair electron. However, the effects of temperature uniformly affect the molecular interaction.

Internal pressure is one of the effective parameters to explain the nature and strength of intermolecular forces existing between molecules. However, in broader concept and contribute to dispersive forces, ionic and dipolar interaction contribute to overall interaction in a liquid system. The value of excess internal pressure shown in Table 7 is negative for both systems and increases with an increase in the mole fraction of both pyridine and toluene. This is due to the existence of dipolar force between unlike molecules.

Table 7. Excess values of acoustic impedance, Gibb's free energy, and internal pressure at different temperatures.

Mole fraction		Excess Acoustic Impedance ($x\ 10^6$)				Excess Gibb's free energy ($x\ 10^{-20}$)				Excess Internal Pressure ($x\ 10^6$)			
X_1	X_2	288K	298K	308K	318K	288K	298K	308K	318K	288k	298K	308K	318K
S-1: DMF + Butanol + Pyridine													
0.12	0.42	1.139	1.156	1.190	1.193	0.028	-0.042	-0.100	-0.147	-4.21	-4.28	-4.13	-4.01
0.21	0.33	1.209	1.398	1.177	1.185	-0.031	-0.198	-0.092	-0.139	-4.37	-4.52	-4.16	-4.03
0.29	0.25	1.491	1.246	1.158	1.196	-0.224	-0.130	-0.101	-0.167	-4.70	-4.50	-4.23	-4.12
0.38	0.16	1.262	1.259	1.144	1.089	-0.118	-0.187	-0.136	-0.119	-4.66	-4.65	-4.36	-4.14
0.47	0.07	1.093	1.138	1.230	1.173	0.030	-0.078	-0.178	-0.174	-4.47	-4.53	-4.41	-4.21
0.54	0.00	1.128	1.198	1.193	1.166	-0.050	-0.135	-0.166	-0.177	-4.69	-4.64	-4.44	-4.25
S-2: DMF + Butanol + Toluene													
0.09	0.45	1.133	1.109	1.078	1.053	-0.122	-0.162	-0.170	-0.185	-3.74	-3.71	-3.48	-3.30
0.19	0.35	1.172	1.124	1.091	1.055	-0.137	-0.155	-0.161	-0.163	-3.93	-3.86	-3.63	-3.43
0.28	0.26	1.155	1.128	1.099	1.076	-0.122	-0.146	-0.155	-0.168	-4.11	-4.01	-3.79	-3.60
0.37	0.17	1.135	1.112	1.069	1.038	-0.094	-0.119	-0.117	-0.123	-4.25	-4.15	-3.92	-3.73
0.46	0.08	1.136	1.114	1.078	1.040	-0.073	-0.095	-0.099	-0.099	-4.39	-4.27	-4.05	-3.86
0.54	0.00	1.128	1.198	1.193	1.166	-0.050	-0.135	-0.166	-0.177	-4.69	-4.64	-4.44	-4.25

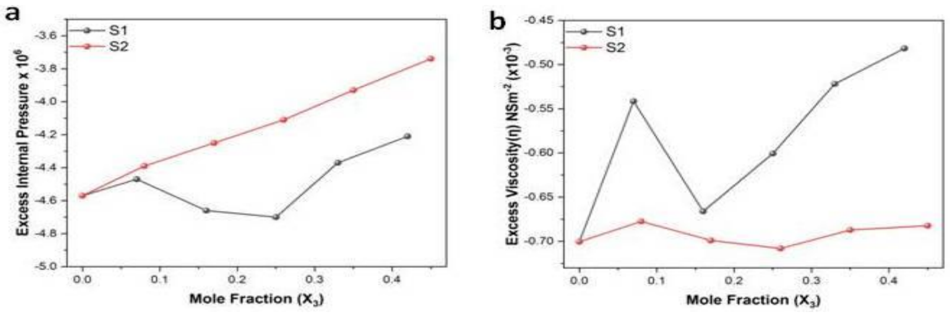


Fig. 4. Variation of excess internal pressure (a) and excess viscosity (b) of both S1 and S2 systems with mole fraction of third components X3.

Excess acoustic impedance increases with the increase in mole fraction of DMF at a constant temperature, and the same acoustic impedance decreases with the rise in temperature at a fixed mole fraction, and it is found to be more for toluene than pyridine.

This decrease in acoustic impedance at higher temperatures is due to thermal agitation, which causes less interaction between the molecules.

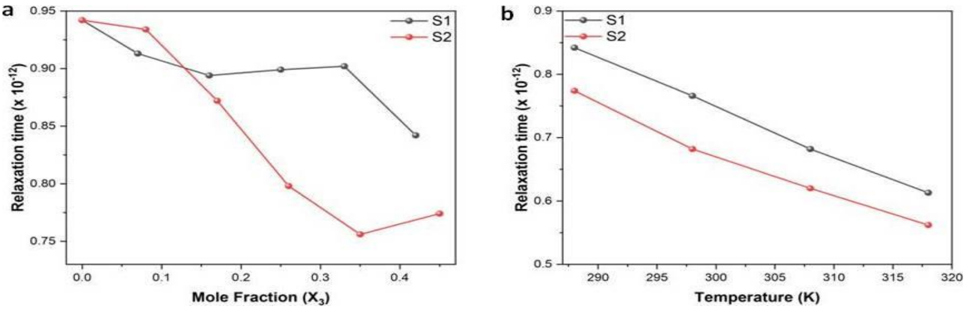


Fig. 5. Variation of relaxation time (a), with mole fraction of third components X_3 and with temperature (b).

Relaxation time increases with an increase in mole fraction of DMF in both systems and in the order of 10^{-12} sec, which is due to the structural relaxation process, and molecules may be rearranged due to the co-operative process. A decrease in relaxation time with an increase in temperature suggests that rearrangement takes place at a faster rate at higher temperatures. The higher value of relaxation time for pyridine than toluene may be due to the fact that interaction between components in DMF-butanol-pyridine is More than DMF-butanol-toluene.

4. Conclusion

It is obvious that there exists a molecular interaction between the components of the ternary mixture, which depends on the dielectric constant and dipole moment of the molecule. The presence of toluene in the binary mixture of butanol and DMF reduces the intermolecular interaction due to its lower dipole moment value. The toluene molecule weakens the existing H-bonded interaction between butanol and DMF. It disperses the molecules away from each other, which is confirmed by the density, viscosity, and other measured and derived parameters. Pyridine provides a H- bonded site due to a lone pair containing a nitrogen atom as well as its high dipole moment value which leads to more interaction between butanol, DMF, and pyridine. However, a change in the trend of molecular interaction at a higher mole fraction is observed in both systems. Due to the presence of lone pair electron, solute polarity is higher in the pyridine system, which was found to regulate the derived parameters concerning change in mole fraction. It is also concluded that the study of density, viscosity, and ultrasonic velocity and the related derived parameters from these, as well as the excess parameters, are a very useful tool for studying the intermolecular interactions between the components in a ternary mixture.

References

1. A. K. Sahoo, S. P. Das, and A. K. Patnaik, Res. Develop. Mater. **12**, ID 000776 (2019).
2. A. K Sahoo, S. K. Pradhan, A. K. Patnaik, and S. P. Das, World J. Pharmaceut. Res. **9**, 1, (2020).
3. M. K. Praharaj, J. Sci. Res. **13**, 1 (2021). http://dx.doi.org/10.3329/jsr.v13i1.44977
4. M. K. Praharaj, A. Satapathy, P. R. Mishra, and S. Mishra, J. Theory Appl. Phys. **7**, 23 (2013). https://doi.org/10.1186/2251-7235-7-23
5. M. K. Praharaj and A. Satapathy, Indian J. Natural Sci. **12**, 65, (2021).
6. M. K. Praharaj, Int. Res. J. Eng. Technol. **7**, 1, (2020),
7. M. K. Praharaj, A. Satapathy, P. R. Mishra, and S. Mishra, J. Chem. Pharm. Res. **5**, 49 (2013).
8. S. Nayak, R. Panigrahi, and B. R. Das, Adv. Sci. Lett. **22**, 301 (2016). https://doi.org/10.1166/asl.2016.6840
9. S. Panda and M. K. Praharaj, Indian J. Natural Sci. **10**, 59 (2020).
10. P. L. Soni, A Text Book of Organic Chemistry (Sultan & Chand Sons Ltd, New Delhi, 1988).
11. S. Thirumaran, K. Jayalakshmi, Achieves Appl. Sci. Res. **1**, 24 (2009).
12. M. K. Praharaj, A. Satapathy, J. Emerg. Technol. Innovat. Res. **6**, 4, (2019).
13. M. K. Praharaj, S. Mishra, J. Thermal Anal. Calorimet. **13** (2018).
14. N. Prasad and H. Rajendra, J. Pure Appl. Ultrasonics **25**, 25 (2003).
15. A. Ali and M. Tariq, Phys. Chem. Liquids **46**, 47 (2008). https://doi.org/10.1080/00319100701344628
16. B. Samantaray, M. K. Praharaj, and S. P. Das, J. Ultra Chem. **17**, 1 (2021). https://doi.org/10.22147/juc/170101
17. A. J. Vogal, Practical Organic Chemistry, 4th Edition (Longman, London, 1978).
18. D. N. Rao, A. Krishnaiah, P. R. Naidu, Acta.Chim. Acad. Sci. Hung. **107**, 49 (1981).
19. P. S. Nikam, M. Hasan, Asian J. Chem. **5**, 319 (1993).
20. A. Ali, A. K. Nain, and M. Kamil, Thermochemica Acta, **274**, 209 (1996). https://doi.org/10.1016/0040-6031(95)02719-X
21. I. Saxena, R. N. Pathak, V. Kumar, and R. Devi, Int. J. App. Res. **1**, 562 (2015).
22. N. Prasad, J. Pure. App. Ultrasonics **25**, 25 (2003).
23. R. Palani and S. Balakrishnan, Ind. J. Pure Appl. Phys. **48**, 544 (2010).
24. R. Varada, A. Sreenivasulu, and G. Raghuraman, Ind. J. Chem. Tech. **1**, 302 (1994).
25. A. M. E. Raj, L. B. Resmia, V. Bena Jothyb, M. Jayachandranc, and C. Sanjeeviraja, Fluid Phase Equilibria **281**, 78 (2009). https://doi.org/10.1016/j.fluid.2009.04.009
26. D. S. Kumar and D. K. Rao., Indian J. Pure Appl. Phys. **45**, 210 (2007).
27. W. Schaaffs and M. Akustik (Spinger-Verlag, Berlin, 1963). https://doi.org/10.1007/978-3-642-87538-0
28. K. Raja1, D. Chinnarao, M. Srilatha, C. Padmarao, and B. V. Rao, Int. J. Eng. Res. Technol. **8**, 10 (2019).
29. R. J. Fort and W. R. Moore, Trans. Faraday Soc. **62**, 1112, (1966).