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Acoustical and Excess Thermodynamic Studies of Some Ketones with DMSO in Primary Alcohol at Varying Temperatures

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ABSTRACT

Densities, viscosities and speed of sound for the four ternary liquid mixtures of ketones such as Acetophenone, Diethyl Ketone, Acetone and cyclohexanone with Dimethyl Sulfoxide in 1-Proponol were measured as a function of mole fraction at 303K, 308K and 313K at atmospheric pressure. From these measurements, excess values of adiabatic compressibility(β^E), free length(L_f^E), free volume(V_f^E), internal pressure(π_i^E), Gibbs free energy ($\Delta G*^E$) and viscosity(η^E) were evaluated. The excess values were found to be almost negative throughout the whole range of composition for all the four liquid systems. The Grunberg's Interaction parameter (d) was also evaluated in order to ascertain the conclusions drawn from these evaluated excess parameters. The addition of DMSO with ketones resulting in rupture of dipoles between unlike molecules. The present investigation notices a weak molecular interaction in the liquid mixtures. The varying temperature also plays a vital role in weakening of the molecular interaction between unlike molecules.

KEYWORDS: DMSO, Ketones, Excess properties, Molecular interactions, Interaction Parameter

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INTRODUCTION

Ultrasonic speed plays an important role in the investigation of intermolecular interactions. The structural arrangements are influenced by the shape of the molecules as well as by their mutual interactions[1]. Ultrasonic studies of binary mixtures or ternary mixtures have been preferred in many diversifying fields such as scattering spectroscopy and biomedical research. Furthermore, in the chemical industry, information on density and viscosity of the liquid mixtures are vital in different applications that include surface facilities, pipeline systems and mass transfer operations.

The present investigation related to thermodynamic properties of ternary liquid mixtures containing DMSO, which is aprotic, strongly associated due to highly polar S=O group molecule, large dipole moment and dielectric constant. The other components of ternary mixtures belonging to ketone series have a common functional group C=O. While acetone and DEK falling under the category of aliphatic series, acetophenone is an aromatic compound and cyclohexanone is cyclic. All these ketones are aprotic molecules having large dipole moment values and possessing high polarizability values too. In addition to this, Acetone is known to be extensively self-associated through H-bonding in the pure state.

DMSO was particularly chosen because of its wide range of applicability as a solvent in synthetic chemistry (Carbohydrates, dyes, resins, polymers) in biological process and in pharmacy and medicine (dermatology, immunology, microbiology). DMSO exhibits dipole-dipole interactions in the pure state because of its fairly high dipole moment and dielectric constant. However,the association between alcohol molecules, which are strongly associated in the pure state through hydrogen bonding to form aggregates. Alcohols represent an important class of hydrogen-bonded solvents, for which the degree of association is very sensitive to temperature as well as to the carbon chain length[2]. The thermodynamic properties of ternary systems of DMSO with alcohols and ketones depend on the interactions between the sulfoxide group (S=O) of DMSO and the hydroxyl (-OH) or carbonyl (C=O) group of alcohol or ketone, respectively. Such a database, which concerns thermodynamic properties of ternary mixtures of DMSO with alcohols and ketones, will have great relevance in the engineering process as well as in other industrial sectors. Ketones are organic compounds that contain a carbonyl group and two aliphatic or aromatic substituents containing the chemical formula $RCOR^1$. Here R and R^1 may be same or different incorporated into a ring (alkyl, aryl and heterocyclic radicals)[3]. The chemical reactivity of the carbonyl group (C=O) plays vital role in chemical reactions and is influenced considerably by steric effects. The greater electro negativity

of O- and high dipole moment makes ketones polar[4]. The thermodynamic properties of ternary systems of DMSO with alcohols and ketones depend on the interactions between the sulfoxide group (S=O) of DMSO and the hydroxyl (-OH) or carbonyl (C=O) group of alcohol or ketone respectively. Such a database, which concerns thermodynamic properties of ternary mixtures of DMSO with alcohols and ketones, will have great relevance in the engineering process as well as in other industrial sectors.

Dimethyl sulphoxide (DMSO) and ketones are important liquids that find a variety of applications such as solvents for lacquers, oils and resins. The properties of DMSO, which is a highly polar solvent, have been the subject of considerable interest because of its versatility as a solvent and a plasticizer[5]. Several researchers clearly elucidated in the literature for the ultrasonic studies of binary mixtures of (DMSO + aromatic/ aliphatic hydrocarbons[6], + some alkanols[7], + water[8], +N, N-dimethylformamide or N, N-dimethylacetamide[9], + aromatic hydrocarbons[10]). However, the probing of molecular interactions between ternary liquid mixtures of DMSO and ketones in the presence of primary alcohol which are scarcely seen. In order to characterize the nature and magnitude of the molecular interactions involving DMSO with ketones namely acetophenone, diethyl ketone, acetone and cyclohexanone along with alcohol (1-propanol), the present investigation has been carried out at varying temperatures of 303K,308K and 313K and at atmospheric pressure.

The four ternary liquid systems taken up for study at 303K, 308K and 313K are

System-I   Dimethyl Sulfoxide (DMSO)+ 1-Proponol + Acetophenone (AP)

System-II   Dimethyl Sulfoxide (DMSO) + 1-Proponol + Diethyl Ketone (DEK)

System-III   Dimethyl Sulfoxide (DMSO) + 1-Proponol + Acetone(AC)

System-IV   Dimethyl Sulfoxide (DMSO) + 1-Proponol + Cyclohexanone(CH)

1. Experimental Section

The chemicals used in the present work were analytical reagent (AR) and spectroscopic reagent (SR) grades with minimum assay were used. In all systems, the various concentrations of the ternary liquid mixtures were prepared in terms of mole fraction, out of which the mole fraction of the second component 1-Proponol ($X_2 = 0.4$) was kept fixed while the mole fractions of the remaining two components DMSO (X_1) and Ketones (X_3) were varied from 0.0 to 0.6. There is nothing significant in fixing the second component at 0.4 mole fraction. The density of pure liquids and liquid mixtures are determined using a specific gravity bottle of 5 ml capacity by relative

measurement method with an accuracy of ± 0.1mg (Model: SHIMADZU AX 200).An Ostwald's viscometer of 10ml capacity is used for the viscosity measurement of pure liquids and Liquid mixtures. The viscometer is calibrated with fresh conductivity water immersed in the water bath which is kept at the experimental temperature. The time of flow (t_w) of water and the time flow (t_s) of solution is measured with digital stop clock having an accuracy of 0.01s (Model: RACER HS-10W) An ultrasonic interferometer (Model: F-81) supplied by M/s. Mittal Enterprises, New Delhi, having the frequency 2MHz with an overall accuracy of ± 2 ms^{-1} has been used for velocity measurement.

2. Results and Discussion

In the present study, the values of density (ρ), viscosity (η) and the ultrasonic wave velocity (U) are tabulated in Tables1 to 4. The excess values of viscosity(η^E), adiabatic compressibility(β^E), free length(L_f^E), free volume(V_f^E), internal pressure(π_i^E), Gibbs Energy(ΔG^{*E}) and Grunberg and Nissan's interaction parameter(d) are listed in Tables 5 to 16.

Table 1: Values of Density (ρ), Viscosity (η) and Ultrasonic velocity (U) of System-I

| Mole Fraction | | Density ρ/(kg/m$^{3)}$) | | | Viscosity η/(x 10^{-3} NSm^{-2}) | | | Ultrasonic Velocity U/(m/s) | | |
| | | Temperature (K) | | | | | | | | |
X$_1$	X$_3$	303	308	313	303	308	313	303	308	313
0.0000	0.5999	927.23	918.33	915.99	1.2014	1.1090	1.0244	1350.3	1338.6	1328.4
0.1136	0.4821	935.20	925.31	922.39	1.2590	1.1382	1.0578	1351.8	1339.7	1329.7
0.2000	0.4002	942.40	933.72	930.59	1.2901	1.1943	1.1015	1354.3	1342.1	1330.9
0.2998	0.2999	949.19	940.11	937.59	1.3180	1.2169	1.1326	1355.2	1342.7	1331.2
0.3995	0.2000	956.78	947.30	944.58	1.3345	1.2316	1.1431	1356.6	1343.9	1332.1
0.5096	0.1017	967.09	958.17	954.27	1.3585	1.2622	1.1597	1359.8	1345.9	1333.8
0.6035	0.0000	972.38	963.06	960.58	1.3646	1.2687	1.1813	1360.2	1347.7	1334.5

Table 2: Values of Density (ρ), Viscosity (η) and Ultrasonic velocity (U) of System-II

| Mole Fraction | | Density ρ/(kg/m³) | | | Viscosity η/(x 10⁻³ NSm⁻²) | | | Ultrasonic Velocity U/(m/s) | | |
| | | Temperature (K) | | | | | | | | |
X_1	X_3	303	308	313	303	308	313	303	308	313
0.0000	0.5716	798.44	795.82	786.46	0.5399	0.5050	0.4719	1194.2	1179.2	1166.8
0.1000	0.5000	827.67	819.72	815.25	0.6228	0.5823	0.5441	1222.5	1207.2	1194.1
0.1999	0.3999	856.20	848.13	844.63	0.6992	0.6520	0.6113	1249.0	1234.9	1221.7
0.3003	0.2988	885.25	876.67	872.82	0.8333	0.7786	0.7213	1276.7	1262.6	1249.3
0.4041	0.1915	914.17	906.20	902.21	0.9805	0.9020	0.8282	1305.0	1291.7	1278.2
0.4998	0.1000	942.01	933.42	930.80	1.1306	1.0554	0.9788	1330.9	1318.0	1304.3
0.6035	0.0000	972.38	963.06	960.58	1.3646	1.2687	1.1813	1360.2	1347.7	1334.5

Table 3: Values of Density (ρ), Viscosity(η) and Ultrasonic velocity(U) of System-III

| Mole Fraction | | Density ρ/(kg/m³) | | | Viscosity η/(x 10⁻³ NSm⁻²) | | | Ultrasonic Velocity U/(m/s) | | |
| | | Temperature (K) | | | | | | | | |
X_1	X_3	303	308	313	303	308	313	303	308	313
0.0000	0.6000	784.35	775.74	769.87	0.4483	0.4166	0.3927	1160.0	1149.5	1136.2
0.1193	0.5027	822.76	813.02	808.25	0.5322	0.4975	0.4653	1204.3	1193.6	1182.5
0.1999	0.4000	846.56	837.12	832.04	0.6240	0.5866	0.5512	1227.2	1215.2	1202.6
0.2999	0.2998	877.74	868.78	864.12	0.7712	0.7144	0.6655	1260.4	1248.1	1235.3
0.4277	0.1443	917.96	908.09	904.81	0.9244	0.8606	0.8003	1304.6	1292.6	1279.8
0.5167	0.0697	945.16	936.58	932.99	1.1157	1.0392	0.9718	1335.5	1321.2	1307.9
0.6035	0.0000	972.38	963.06	960.58	1.3646	1.2687	1.1813	1360.2	1347.7	1334.5

Table 4: Values of Density (ρ), Viscosity (η) and Ultrasonic velocity (U) of System-IV

Mole Fraction		Density ρ/(kg/m³)			Viscosity η/(x 10⁻³ NSm⁻²)			Ultrasonic Velocity U/(m/s)		
		Temperature (K)								
X_1	X_3	303	308	313	303	308	313	303	308	313
0.0000	0.6000	878.91	869.41	864.64	0.9187	0.8712	0.8326	1319.0	1312.1	1310.3
0.1111	0.4436	889.13	879.14	875.33	0.9826	0.9444	0.9099	1327.4	1319.6	1315.1
0.1998	0.3999	909.14	900.16	896.07	1.0782	1.0247	0.9916	1332.8	1323.8	1317.7
0.2997	0.3000	924.86	915.53	911.14	1.1709	1.0860	1.0682	1339.3	1329.4	1321.6
0.3999	0.2001	940.17	930.42	927.47	1.2392	1.1355	1.1276	1346.0	1335.2	1325.6
0.5005	0.0999	956.19	946.52	943.49	1.3000	1.2278	1.1582	1353.2	1341.6	1330.2
0.6035	0.0000	972.38	963.06	960.58	1.3646	1.2687	1.1813	1360.2	1347.7	1334.5

The present study observes that the values of density (ρ), viscosity (η) and the ultrasonic wave velocity (U) increases with addition of ketones. The variation of ultrasonic velocity in a mixture depends upon the increase (or) decrease of intermolecular free length after mixing the components. According to Erying and Kincaid[11], 1938 for sound projection, ultrasonic wave velocity should decrease, if the intermolecular free length increase and vice-versa. This is ascertained in the present investigation for all the four liquid systems. Further, it is interesting to note that density, viscosity and ultrasonic velocity values decrease with increase of temperature.

As the increasing values of density, viscosity and ultrasonic velocity with composition of DMSO with ketones in the presence of 1-propanol, suggesting that the dipole-dipole interactions are existing in the ternary mixtures. The decreasing of ultrasonic velocity, density and viscosity with increases of temperature reveals that at higher temperature the molecular interactions between the component molecules are weakened due to thermal dispersion forces are existing in the liquid mixtures. The similar trend has been observed by earlier workers[12].

The thermodynamic excess properties of organic liquid mixtures depend on the chemical structure, size and shape of their constituent molecules. The excess functions which are a measure of deviation from ideal behaviour are found to be highly sensitive to intermolecular interactions

between component molecules of the mixtures. The sign and magnitude of these functions depend on the strength of interaction between dissimilar molecules in the mixture.

Table 5: Excess values of Viscosity (η^E), Adiabatic compressibility (β^E) of System-I

Mole Fraction		Excess Viscosity η^E/(x 10^{-3} NSm^{-2}) Temperature(K)			Excess Adiabatic compressibility β^E/(x10^{-10}m^{2}N^{-1})		
X_1	X_3	303	308	313	303	308	313
0.0000	0.5999	-0.4292	-0.2506	-0.2367	-0.3811	-0.3807	-0.3789
0.1136	0.4821	-0.3659	-0.2471	-0.2218	-0.4201	-0.4136	-0.4085
0.2000	0.4002	-0.3596	-0.2100	-0.1925	-0.4377	-0.4366	-0.4233
0.2998	0.2999	-0.3606	-0.2092	-0.1774	-0.4495	-0.4415	-0.4319
0.3995	0.2000	-0.3735	-0.2166	-0.1832	-0.4604	-0.4566	-0.4476
0.5096	0.1017	-0.3794	-0.2191	-0.1847	-0.4773	-0.4656	-0.4509
0.6035	0.0000	-0.4027	-0.2245	-0.1885	-0.4991	-0.4842	-0.4721

Table 6: Excess values of Viscosity (η^E) and Adiabatic compressibility (β^E) of System-II

Mole Fraction		Excess Viscosity η^E/(x 10^{-3} NSm^{-2}) Temperature (K)			Excess Adiabatic compressibility β^E/(x10^{-10}m^{2}N^{-1})		
X_1	X_3	303	308	313	303	308	313
0.0000	0.5716	-0.4341	-0.3350	-0.2824	-0.0752	-0.0702	-0.0636
0.1000	0.5000	-0.4525	-0.3419	-0.2902	-0.1779	-0.1676	-0.1500
0.1999	0.3999	-0.5146	-0.3860	-0.3280	-0.3381	-0.3182	-0.2971
0.3003	0.2988	-0.5202	-0.3742	-0.3240	-0.4557	-0.4464	-0.4365
0.4041	0.1915	-0.5213	-0.3726	-0.3292	-0.5106	-0.5021	-0.4929
0.4998	0.1000	-0.4979	-0.3235	-0.2752	-0.5196	-0.4848	-0.4730
0.6035	0.0000	-0.4027	-0.2245	-0.1885	-0.4991	-0.4842	-0.4721

Table 7: Excess values of Viscosity (η^E) and Adiabatic compressibility (β^E) of System-III

Mole Fraction		Excess Viscosity $\eta^E/(\ x\ 10^{-3}\,NSm^{-2})$			Excess Adiabatic compressibility $\beta^E/(\ x10^{-10}m^2N^{-1})$		
		Temperature(K)					
X_1	X_3	303	308	313	303	308	313
0.0000	0.6000	-0.4163	-0.3244	-0.2714	-0.0420	-0.0320	-0.0140
0.1193	0.5027	-0.5222	-0.4826	-0.4136	-0.3413	-0.3204	-0.3166
0.1999	0.4000	-0.5414	-0.4050	-0.3446	-0.5090	-0.4863	-0.4760
0.2999	0.2998	-0.5447	-0.4026	-0.3461	-0.6057	-0.5955	-0.5841
0.4277	0.1443	-0.6231	-0.3985	-0.3868	-0.6122	-0.6087	-0.5900
0.5167	0.0697	-0.5453	-0.3649	-0.3042	-0.5791	-0.5764	-0.5655
0.6035	0.0000	-0.4027	-0.2245	-0.1885	-0.4991	-0.4842	-0.4721

Table 8: Excess values of Viscosity (η^E) and Adiabatic compressibility (β^E) of System-IV

Mole Fraction		Excess Viscosity $\eta^E/(\ x\ 10^{-3}\,NSm^{-2})$			Excess Adiabatic compressibility $\beta^E/(\ x\ 10^{-10}m^2N^{-1})$		
		Temperature(K)					
X_1	X_3	303	308	313	303	308	313
0.0000	0.6000	-0.7519	-0.5817	-0.4421	-0.2196	-0.2006	-0.1931
0.1111	0.4436	-0.8092	-0.6725	-0.5273	-0.3250	-0.3128	-0.3037
0.1998	0.3999	-0.6628	-0.5021	-0.3681	-0.3406	-0.3382	-0.3375
0.2997	0.3000	-0.5764	-0.4322	-0.2912	-0.3902	-0.3863	-0.3731
0.3999	0.2001	-0.5146	-0.3742	-0.2307	-0.4316	-0.4210	-0.4128
0.5005	0.0999	-0.4597	-0.2741	-0.2011	-0.4796	-0.4665	-0.4543
0.6035	0.0000	-0.4027	-0.2245	-0.1885	-0.4991	-0.4842	-0.4721

Table 9: Excess values of Intermolecular free length (L_f^E) and Free volume (V_f^E) of System-I

Mole Fraction		Excess Intermolecular free length $L_f^E/(\ x10^{-10}m)$			Excess Free volume $V_f^E/(\ x10^{-7}m^3\ mol^{-1})$		
		Temperature(K)					
X_1	X_3	303	308	313	303	308	313
0.0000	0.5999	-0.0088	-0.0078	-0.0069	0.2974	0.2251	0.2125
0.1136	0.4821	-0.0101	-0.0098	-0.0078	0.2193	0.1856	0.1729
0.2000	0.4002	-0.0112	-0.0106	-0.0083	0.1908	0.1366	0.1166
0.2998	0.2999	-0.0122	-0.0115	-0.0102	0.1742	0.1166	0.1069
0.3995	0.2000	-0.0134	-0.0128	-0.01127	0.1711	0.1191	0.1012
0.5096	0.1017	-0.0144	-0.0133	-0.01276	0.1751	0.1728	0.1440
0.6035	0.0000	-0.0125	-0.0117	-0.0115	0.1926	0.1463	0.1457

Table 10: Excess values of Intermolecular free length (L_f^E) and Free volume (V_f^E) of System-II

| Mole Fraction		Excess Intermolecular free length $L_f^E/(\ x10^{-10}m)$			Excess Free volume $V_f^E/(\ x10^{-7}m^3\ mol^{-1})$		
		Temperature(K)					
X_1	X_3	303	308	313	303	308	313
0.0000	0.5716	-0.0026	-0.0024	-0.0023	-0.0282	-0.0582	-0.0945
0.1000	0.5000	-0.0038	-0.0037	-0.0035	-0.3576	-0.3657	-0.3858
0.1999	0.3999	-0.0075	-0.0074	-0.0072	-0.2718	-0.2959	-0.3067
0.3003	0.2988	-0.0107	-0.0106	-0.0104	-0.2356	-0.2517	-0.2655
0.4041	0.1915	-0.0122	-0.0112	-0.0106	-0.1346	-0.1400	-0.1768
0.4998	0.1000	-0.0126	-0.0123	-0.0121	0.0190	0.0701	0.0450
0.6035	0.0000	-0.0125	-0.0117	-0.0115	0.1926	0.1463	0.1457

Table 11: Excess values of Intermolecular free length (L_f^E) and Free volume (V_f^E) of System-III

Mole Fraction		Excess Intermolecular free length L_f^E/(x10^{-10}m)			Excess Free volume V_f^E/(x10^{-7}m^3 mol^{-1})		
		Temperature(K)					
X_1	X_3	303	308	313	303	308	313
0.0000	0.6000	-0.0014	-0.0007	-0.0005	-0.2446	-0.2558	-0.2681
0.1193	0.5027	-0.0069	-0.0067	-0.0065	-0.1266	-0.1367	-0.1432
0.1999	0.4000	-0.0110	-0.0108	-0.0107	-0.1892	-0.2209	-0.2391
0.2999	0.2998	-0.0138	-0.0137	-0.0121	-0.1852	-0.2091	-0.2278
0.4277	0.1443	-0.0150	-0.0144	-0.0142	-0.1254	-0.2017	-0.2714
0.5167	0.0697	-0.0144	-0.0140	-0.0137	0.1562	0.1248	0.1178
0.6035	0.0000	-0.0125	-0.0117	-0.0115	0.1926	0.1463	0.1457

Table 12: Excess values of Intermolecular free length (L_f^E) and Free volume (V_f^E) of System-IV

Mole Fraction		Excess Intermolecular free length L_f^E/(x10^{-10}m)			Excess Free volume V_f^E/(x10^{-7}m^3 mol^{-1})		
		Temperature(K)					
X_1	X_3	303	308	313	303	308	313
0.0000	0.6000	-0.0045	-0.0044	-0.0041	0.8884	0.8687	0.8566
0.1111	0.4436	-0.0076	-0.0073	-0.0070	0.6876	0.6614	0.6063
0.1998	0.3999	-0.0079	-0.0077	-0.0073	0.5271	0.5071	0.4402
0.2997	0.3000	-0.0093	-0.0092	-0.0087	0.3857	0.3523	0.3030
0.3999	0.2001	-0.0105	-0.0098	-0.0093	0.3093	0.2900	0.2161
0.5005	0.0999	-0.0121	-0.0114	-0.0112	0.1952	0.1951	0.1742
0.6035	0.0000	-0.0125	-0.0117	-0.0115	0.1926	0.1463	0.1457

An examination of data in Tables 5 to 12 show that the excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) exhibit negative deviations in all the four ternary liquid

systems over the entire range of composition and decreases with molar concentration of ketones. According to Sri Devi et al., 2004[13], negative excess values are due to closely packed molecules which accounts for the existence of strong molecular interactions, whereas positive excess values reflect weak interactions between unlike molecules. The sign of the excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) are useful in assessing the compactness due to molecular interactions in liquid mixtures through hydrogen-bonding, charge transfer, dipole–dipole and dipole-induced dipole interactions, interstitial accommodation and orientationally ordering (Fort and Moore, 1965)[14].The negative values of the excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) in the present systems suggesting an enhanced molecular interactions present between unlike molecules in the liquid mixtures.

The decreasing negative values of excess adiabatic compressibility values, which have been found for the ternary mixtures of DMSO with alcohol (1-propanol) and ketones suggest the strongest association occurs in the greatest available surface area for interaction with the S=O group of DMSO, compared to–OH or C=O groups of alcohol and ketones respectively. However, the decrease of negative value of excess adiabatic compressibility resulting in the expected decrease of the –OH group proton donor capacity of the alcohol, and indicating the strength of the interactions involving with alcohol weakened with the addition of ketones.
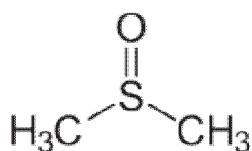
Structure of DMSO

It is attributed that the addition of ketone molecules such as AP, DEK, AC and CH to DMSO will induce breaking of clusters of DMSO molecules thereby releasing several dipoles, which interact with dipoles of ketone. This causes an increase in free space, decrease in sound velocity and negative deviation in adiabatic compressibility. This effect will be counteracted due to the interaction between carbonyl group of ketone and S=O group of DMSO, which changes in free volume in the real mixtures and interstitial accommodation of component molecules into each other's structure resulting in weakening of molecular association between unlike molecules.

Table 13: Excess values of Internal pressure (π_i^E) and Gibb's free energy ($\Delta G*^E$) of System-I

Mole Fraction		Excess Internal pressure $\pi_i^E/(\times 10^6 \, Nm^{-2})$ Temperature(K)			Excess Gibb's free energy $\Delta G*^E/(\times 10^{-20} \, KJ \, mol^{-1})$		
X_1	X_3	303	308	313	303	308	313
0.0000	0.5999	-110.2842	-108.0907	-107.2390	-0.1209	-0.0980	-0.0949
0.1136	0.4821	-115.9911	-114.2370	-112.4744	-0.1117	-0.0939	-0.0897
0.2000	0.4002	-119.1739	-107.4060	-103.5352	-0.1085	-0.0792	-0.0789
0.2998	0.2999	-121.0014	-102.1951	-95.3611	-0.1069	-0.0760	-0.0734
0.3995	0.2000	-120.6380	-94.7927	-88.0057	-0.1096	-0.0767	-0.0762
0.5096	0.1017	-112.9901	-76.9586	-74.3359	-0.1099	-0.0821	-0.0794
0.6035	0.0000	-104.5713	-60.3325	-52.7149	-0.1164	-0.0767	-0.0755

Table 14: Excess values of Internal pressure (π_i^E) and Gibb's free energy ($\Delta G*^E$) of System-II

Mole Fraction		Excess Internal pressure $\pi_i^E/(\times 10^6 \, Nm^{-2})$ Temperature(K)			Excess Gibb's free energy $\Delta G*^E/(\times 10^{-20} \, KJ \, mol^{-1})$		
X_1	X_3	303	308	313	303	308	313
0.0000	0.5716	-157.2218	-132.2604	-123.5982	-0.1414	-0.1310	-0.1261
0.1000	0.5000	-163.0071	-126.7534	-117.1995	-0.1382	-0.1287	-0.1178
0.1999	0.3999	-166.9298	-132.6719	-122.5370	-0.1371	-0.1256	-0.1128
0.3003	0.2988	-158.8136	-121.8307	-114.2335	-0.1358	-0.1130	-0.1123
0.4041	0.1915	-150.7346	-114.3098	-109.4739	-0.1345	-0.1108	-0.1089
0.4998	0.1000	-136.7538	-93.8112	-86.1989	-0.1264	-0.0986	-0.0954
0.6035	0.0000	-104.5713	-60.3325	-52.7149	-0.1164	-0.0767	-0.0755

**Table 15: Excess values of Internal pressure (π_i^E) and Gibb's free energy (ΔG^{*E}) of System-III**

Mole Fraction		Excess Internal pressure $\pi_i^E/(\text{ x }10^6 \text{Nm}^{-2})$			Excess Gibb's free energy $\Delta G^{*E}/(\text{ x}10^{-20} \text{ KJ mol}^{-1})$		
		Temperature(K)					
X_1	X_3	303	308	313	303	308	313
0.0000	0.6000	-123.5226	-99.7897	-91.7945	-0.1200	-0.1127	-0.1088
0.1193	0.5027	-182.0404	-146.8018	-137.2504	-0.1954	-0.1774	-0.1742
0.1999	0.4000	-159.3246	-117.1879	-108.8515	-0.1617	-0.1570	-0.1473
0.2999	0.2998	-139.8873	-106.0661	-97.5507	-0.1393	-0.1287	-0.1192
0.4277	0.1443	-137.3319	-98.7750	-84.0842	-0.1356	-0.1152	-0.1139
0.5167	0.0697	-132.1085	-93.3815	-81.6515	-0.1226	-0.1096	-0.1052
0.6035	0.0000	-104.5713	-60.3325	-52.7149	-0.1164	-0.0767	-0.0755

Table 16: Excess values of Internal pressure (π_i^E) and Gibb's free energy (ΔG^{*E}) of System-IV

Mole Fraction		Excess Internal pressure $\pi_i^E/(\text{ x }10^6 \text{Nm}^{-2})$			Excess Gibb's free energy $\Delta G^{*E}/(\text{ x}10^{-20} \text{ KJ mol}^{-1})$		
		Temperature(K)					
X_1	X_3	303	308	313	303	308	313
0.0000	0.6000	-215.7034	-183.8563	-160.0356	-0.2554	-0.2442	-0.2200
0.1111	0.4436	-212.5675	-170.9517	-145.8104	-0.2360	-0.2191	-0.2021
0.1998	0.3999	-184.4294	-145.5440	-120.8053	-0.1867	-0.1731	-0.1599
0.2997	0.3000	-162.3668	-127.4090	-99.2962	-0.1727	-0.1467	-0.1378
0.3999	0.2001	-129.4189	-110.7458	-84.8291	-0.1507	-0.1269	-0.1259
0.5005	0.0999	-126.7092	-80.5205	-66.7972	-0.1348	-0.1037	-0.1012
0.6035	0.0000	-104.5713	-60.3325	-52.7149	-0.1164	-0.0767	-0.0755

The perusal of Tables 9 to 12 provides a qualitative picture of excess free volume (V_f^E) values for all the four ternary liquid systems. The excess values are negative in liquid systems II & III, whereas it is found reversed in other two systems. These negative deviations found to be increased with addition of molar concentration of ketones. The sign of the V_f^E depends on the

relative strength between the contractive forces and expansive forces. The factors responsible for volume contraction are (i) specific interactions between the component molecules and (ii) weak physical forces, such as dipole-dipole or dipole-induced dipole interactions or Vander Waal's forces. The factors that cause expansion in volume are dispersive forces, steric hindrance of component molecules, unfavorable geometric fitting and electrostatic repulsion. The present increasing trend of negative values of excess free volume asserts that the effect of the factors responsible for volume expansion leading to weakening of molecular association[15]. Further, the observed negative values suggesting the existence of dipole-dipole interactions between unlike molecules and also the formation of Hydrogen bonds between the oxygen atom of the carbonyl group[16] of ketones and S=O group of DMSO.

In the present liquid mixtures, the study of internal pressure may give some suitable information regarding the nature and strength of the forces existing between the molecules. In fact, the internal pressure is a broader concept and it is a measure of the totality of forces of the dispersion, ionic and dipolar interaction that contribute to be overall cohesion of the liquid systems. The values of excess internal pressure are negative in all the four liquid systems and are increasing with addition of ketones indicating that the dipolar forces are operating between the unlike molecules. Further, the observed increasing negative values of excess internal pressure values advocating the weakening of cohesive forces.

In the present study, the increasing negative values of excess free volume and internal pressure suggest the possibility of loss of dipolar association (dispersion forces) between DMSO and ketone molecules. This implies that the presence of larger $-CH_3 - CH_2 -$ chain attached to carbonyl group of aliphatic ketone causes much more steric hindrance to DMSO over the other ketones leading to elevation of negative values of excess free volume and internal pressure. Thus, dispersion forces and steric hindrance of physical interactions play a vital role in weakening the interactions existing between the unlike molecules[17].
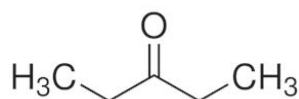
Structure of Diethyl ketone

The reported values in Table 13 to 16 providing the variation of excess Gibbs free energy (ΔG^E) for the four ternary liquid systems. The values of ΔG^E are all negative in all the liquid systems and increase with molar concentration of ketones as well as rise of temperature. According to Read et al., 1965[18], the positive values of excess Gibbs energy values may be attributed to specific interactions like hydrogen bonding and charge transfer, while negative ΔG^E values may be due to the dominance of dispersion forces[19].In the present investigation, it is noticed that the increasing negative values of ΔG^E suggesting the strength of interaction gets weakened on the addition of ketones. It is also learnt from the present study that the behaviour of negative deviation over the elevation of temperature paving the way for weakening of the molecular association as it causes rupture of more hydrogen bonded between unlike molecules.

According to Fort et al.,[14] the study of excess viscosity (η^E) provides information about the strength of molecular interaction between the unlike molecules. For the liquid systems, where dispersion, induction, and dipolar forces which are operated by the values of excess viscosity make the negative, whereas the existence of specific interactions leading to the formation of complexes and hydrogen bonding in liquid mixtures tends to make excess viscosity positive. The evaluated excess viscosity values possessing the negative values in all the four ternary liquid systems and increase with the addition of ketones as well as temperature. The trend of excess viscosity reveals the presence of weak dipolar forces in the liquid mixtures. The increasing negative values of η^E also suggesting the dominance of dispersive interaction resulting from the breaking up of the sulfoxide group (S=O) of DMSO. Further, the increasing negative deviations over the elevation of temperature in all the four liquid systems clearly indicating the strength of interaction gets weakened as thermal dispersion forces are highly operative in the liquid mixtures.

This present investigation eventually may be interpreted as, when ketones such as AP, DEK, AC and CH are mixed with DMSO, the strength of the interaction between the participating molecules depend on the dipole moment or polarizability and geometry (steric hindrance) of the interacting molecules. It is evident that DMSO and the present ketones are polar and their dipole moments value follows as μ_{AC}=2.69D<μ_{DEK}=2.70D<μ_{AP}=3.05D<μ_{CH}=3. 06D.As the difference between dipole moment values of the ketones increases, strength of the interaction decreases. This implies that the presence of larger $-CH_3 - CH_2-$chain attached to carbonyl group of aliphatic ketone causes much more steric hindrance to DMSO over other ketones leading to possession of increasing negative excess values of all parameters. Thus, in the present study, dispersion forces and steric hindrance play a greater role in weakening of molecular association in the liquid systems[20].

Table 17: Values of Grunberg's Interaction parameter (d) of System-I

Mole Fraction (X_1)	Interaction parameter (d)		
	Temperature(K)		
	303	308	313
0.0000	-6.4448	-6.6067	-6.6689
0.1136	-6.4277	-6.5604	-6.6390
0.2000	-6.3785	-6.5307	-6.6198
0.2998	-6.3548	-6.5171	-6.6019
0.3995	-6.3410	-6.5055	-6.5938
0.5096	-6.3397	-6.5012	-6.5922
0.6035	-6.3352	-6.5040	-6.5999

Table 18: Values of Grunberg's Interaction parameter (d) of System-II

Mole Fraction (X_1)	Interaction parameter (d)		
	Temperature(K)		
	303	308	313
0.0000	-7.1732	-7.2814	-7.3631
0.1000	-7.0467	-7.1620	-7.2438
0.1999	-6.8891	-7.0122	-7.0967
0.3003	-6.7373	-6.8742	-6.9614
0.4041	-6.5863	-6.7347	-6.8251
0.4998	-6.4632	-6.6214	-6.7139
0.6035	-6.3352	-6.5040	-6.5999

Table 19: Values of Grunberg's Interaction parameter (d) of System-III

Mole Fraction (X_1)	Interaction parameter (d)		
	Temperature(K)		
	303	308	313
0.0000	-7.4177	-7.5252	-7.5998
0.1193	-7.0429	-7.1603	-7.3580
0.1999	-6.7380	-6.8659	-6.9474
0.2999	-6.8402	-6.9784	-7.0634
0.4277	-6.5682	-6.7273	-6.8193
0.5167	-6.4492	-6.6112	-6.7049
0.6035	-6.3352	-6.5040	-6.5999

Table 20: Values of Grunberg's Interaction parameter (d) of System-IV

Mole Fraction (X_1)	Interaction parameter (d)		
	Temperature(K)		
	303	308	313
0.0000	-6.3593	-6.5138	-6.6008
0.1111	-6.3351	-6.4847	-6.5863
0.1998	-6.3218	-6.4533	-6.5698
0.2997	-6.3124	-6.4408	-6.5652
0.3999	-6.3127	-6.4634	-6.5692
0.5005	-6.3242	-6.4840	-6.5846
0.6035	-6.3352	-6.5040	-6.5999

The existence of weak intermolecular interaction between unlike molecules in the present study further confirmed by evaluating the interaction parameter d in the Gruenberg and Nissan equation which is a measure of strength of interaction between the mixing components. d-values were said to indicate various types of interactions[21]. Large and positive d-values indicate strong specific interaction; small negative values indicate weak specific interaction. It is evident from Tables 17-20 the d-values are negative and increase with addition of mole fraction of ketones. The increasing negative behaviour of d-values advocates weaker interaction between the unlike molecules, and their decreasing trend over the rise of temperature clearly supporting this.

CONCLUSION

Ultrasonic method is a powerful probe for characterising the physico-chemical properties and existence of molecular interactions in liquid mixtures. The present investigation may be consolidated as

> ➢ The evaluated excess values of all parameters suggest a weak dipole-dipole interaction which are existing in the liquid systems.
> ➢ The addition of ketones such as acetophenone, diethyl ketone, acetone and cyclohexanone with dimethyl Sulfoxide induce breaking of its dipoles resulting in weakening of molecular interaction.
> ➢ The increase of temperature too weakens the molecular interaction due to thermal dispersion forces that are operative with liquid mixtures.

> ➢ The strength of molecular interaction among the four-ternary liquid systems are of the order III< II< I< IV

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