Research Article

Thermo physical Properties of Ternary Mixtures of Dimethyl sulphoxide, Benzene, m-Xylene at various Temperatures.

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ABSTRACT

The ultrasonic velocities, densities and viscosities of ternary liquid mixtures of Dimethyl sulphoxide + Benzene + m-Xylene have been determined at different temperatures from 298.15K-313.15K over the whole composition range. The data have been utilized to estimate the excess isentropic compressibility (Ks), excess free length (ΔL_f), excess acoustic impedance (ΔZ), excess volume (ΔVm), excess ultrasonic velocity (ΔU), excess free volume (ΔV_f) and excess viscosity ($\Delta\eta$), at these temperatures. The excess values have been found to be useful in estimating the strength of the interactions in the liquid mixtures. Analysis of these parameters indicates the nature of interaction among the components of the ternary mixtures.

Keywords: DMSO, Ternary mixtures, Excess ultrasonic velocity, Molecular interaction.

INTRODUCTION

The nature and relative strength of the molecular interaction between the components of the liquid mixtures have been successfully investigated by the ultrasonic method[1-3]. These interactions help understand the nature of solute and solvent, i.e., whether the solute modifies or distorts the structure of the solvent.

The measurement of ultrasonic speed enables the accurate determination of some useful acoustical and thermodynamic parameters and their excess functions, which are highly sensitive to molecular interactions in liquid mixtures [4, 5]. Ultrasonic velocity is related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids, binary and ternary mixtures. Many studies have been done to find out the interactions in binary and ternary liquid mixtures by means of acoustic properties, viscometric and thermo dynamical properties of the ternary system [6-10].

The present investigation deals with three important liquids, namely, dimethyl sulphoxide, benzene and m-xylene. The liquids under investigation are very useful chemicals and of industrial significance. Dimethyl sulphoxide (DMSO), which is aprotic, strongly associated due to highly polar S = 0 group molecule and large dipole moment ($\mu = 3.96$) and dielectric constant ($\varepsilon = 46.68$ at 298.15 K). The study of DMSO is very important becauseofit'sutilization in a broad range of applications in medicine. DMSO is well known for its cryoprotective effects on biological systems, because it easily penetrates biological membranes, facilities chemical transport into biological tissues[11-12]. DMSO is also used as free radical scavenger for various cancer treatments. And also most importantly, it is used as a solvent.

MATERIALS AND METHODS

DMSO (E Merck, Germany), Benzene (S.D. Fine Chem, India), purities (mass per cent) >99.5% were used as such without further purification m-xylene (S.D. fine Chem., India, purity> 99%).

The ultrasonic velocities of pure liquids and the ternary mixtures at 298.15K, 303.15K, 308.15K and 313.15K are determined by using ultrasonic interferometer, F-81 Mittal Enterprises, New Delhi at a fixed frequency of 2 MHz. The experimental liquid in the interferometer cell is maintained at the desired temperature ±0.1k by circulating water from the thermostat.

The ternary mixtures of DMSO, benzene and m-xylene were prepared by volume. Nine mixtures were prepared at four different temperatures, 298.15K – 313.15 K. The density values of pure liquids and liquid mixtures have been measured with a specific gravity bottle of 25 ml capacity calibrated at the corresponding temperatures. Similarly, viscosity measurement of ternary solution was covered by out by the Ostwald's glass capillary viscometer at 298.15K, 303.15K, 308.15K, and 313.15K.

Theoretical Aspects

From the ultrasonic velocity (U), density (ρ) and viscosity (η) data, the following parameters have been calculated.

1. The isentropic compressibility (Ks) has been determined by using the experimentally measured ultrasonic velocity (U) and density (ρ) by the following formula.

$$Ks = \frac{1}{\rho U^2} \quad (1)$$

2. Intermolecular free length (L_f) was calculated by using the relation.

$$L_f = K\left(K_s\right)^{1/2} \quad (2)$$

K is temperature independent Jacobson's constant.

3. Acoustic impedance is determined by using the relation.

$$Z = \rho \times U \quad (3)$$

4. Molar volume of ternary mixtures were calculated by using the equation.

$$V_m = \frac{x_1M_1 + x_2M_2 + x_3M_3}{\rho} \quad (4)$$

5. Free volume (V_f) were calculated by the equation

$$V_f = \left(\frac{M_{eff}\,U}{K_a\eta}\right)^{3/2} \quad (5)$$

The excess properties, such as ΔK_s, ΔL_f, ΔZ, ΔV_m, ΔU, ΔV_f and $\Delta\eta$ have been calculated by using the equation.

$$\Delta Y = Y_{exp} - Y_{ideal}$$

$$\Delta Y = Y_{mix} - (x_1Y_1 + x_2Y_2 + x_3Y_3) \quad (6)$$

Where ΔY is ΔK_s, ΔL_f, ΔZ, ΔV_m, ΔU, ΔV_f and $\Delta\eta$.

x represents the mole fraction of the component and subscripts 1 and 2 and 3 stand for the component 1, 2 and 3, respectively.

Table 1: Measured values of density (ρ), Ultrasonic velocity (U) and viscosity (η) and calculated values of isentropic compressibility (Ks), intermolecular free length (L_f), acoustic impedance (Z), molar volume (V_m), free volume (V_f) at temperatures 298-15K -313.15K.

x_1	x_2	x_3	ρ Kgm^{-3}	U m/s	η mpas	K_s 10^{10}N^{-1}m^2	L_f 10^{11}m	Z 10^{-6}Kg m^{-2}s^{-1}	V_m 10^{-5} m^3 mol^{-1}	V_f 10^{6}m^{3}mol^{-1}
298.15K										
0.140	0.500	0.360	897.5	1338.9	0.703	6.22	5.13	1.21	9.83	0.25
0.269	0.423	0.308	929.1	1363.1	0.768	5.79	4.96	1.27	9.34	0.22
0.388	0.354	0.258	955.8	1385.4	0.835	5.46	4.81	1.33	8.94	0.19
0.495	0.292	0.213	994.5	1407.2	0.939	5.08	4.63	1.39	8.46	0.16
0.595	0.234	0.171	1038.8	1426.4	1.045	4.74	4.47	1.49	7.99	0.14
0.688	0.181	0.131	1078.7	1445.1	1.132	4.44	4.34	1.56	7.59	0.13
0.776	0.129	0.095	1127.5	1461.6	1.195	4.16	4.19	1.65	7.17	0.12
0.854	0.084	0.062	1167.9	1478.6	1.288	3.92	4.08	1.73	6.84	0.10
0.931	0.040	0.029	1216.5	1493.7	1.371	3.69	3.95	1.82	6.49	0.10
303.15K										
0.140	0.500	0.360	895.1	1319.1	0.687	6.43	5.26	1.19	9.86	0.25
0.269	0.423	0.308	926.3	1342.9	0.757	5.99	5.08	1.25	9.37	0.22
0.388	0.354	0.258	952.5	1364.4	0.829	5.64	4.93	1.29	8.97	0.19
0.495	0.292	0.213	991.6	1386.4	0.934	5.25	4.76	1.38	8.49	0.16
0.595	0.234	0.171	1035.4	1405.7	1.029	4.89	4.59	1.46	8.01	0.14
0.688	0.181	0.131	1075.4	1424.5	1.101	4.59	4.45	1.54	7.61	0.13
0.776	0.129	0.095	1124.5	1440.6	1.185	4.29	4.29	1.62	7.19	0.11
0.854	0.084	0.062	1165.6	1457.5	1.278	4.04	4.18	1.69	6.86	0.10
0.931	0.040	0.029	1214.5	1471.8	1.331	3.81	4.05	1.79	6.49	0.10
308.15K										
0.140	0.500	0.360	891.1	1300.7	0.675	6.64	5.39	1.16	9.89	0.26
0.269	0.423	0.308	924.9	1325.8	0.745	6.15	5.19	1.23	9.39	0.22
0.388	0.354	0.258	950.4	1347.6	0.813	5.79	5.05	1.29	8.99	0.20
0.495	0.292	0.213	989.4	1370.8	0.929	5.38	4.86	1.36	8.49	0.16
0.595	0.234	0.171	1032.9	1392.1	0.998	4.99	4.69	1.44	8.03	0.15

0.688	0.181	0.131	1071.9	1411.2	1.061	4.69	4.54	1.52	7.64	0.13
0.776	0.129	0.095	1121.8	1427.4	1.153	4.38	4.39	1.61	7.21	0.12
0.854	0.084	0.062	1161.2	1444.6	1.235	4.13	4.26	1.68	6.88	0.11
0.931	0.040	0.029	1211.1	1460.0	1.275	3.88	4.13	1.77	6.52	0.10
313.15K										
0.140	0.500	0.360	888.5	1281.6	0.671	6.86	5.54	1.14	9.93	0.25
0.269	0.423	0.308	921.3	1308.1	0.737	6.35	5.33	1.21	9.42	0.22
0.388	0.354	0.258	948.3	1331.2	0.811	5.96	5.16	1.27	9.01	0.19
0.495	0.292	0.213	986.7	1355.0	0.921	5.52	4.97	1.34	8.53	0.16
0.595	0.234	0.171	1028.1	1377.2	0.991	5.13	4.79	1.42	8.07	0.14
0.688	0.181	0.131	1068.9	1397.8	1.038	4.79	4.63	1.49	7.66	0.14
0.776	0.129	0.095	1118.5	1414.4	1.115	4.47	4.47	1.59	7.23	0.12
0.854	0.084	0.062	1158.1	1432.4	1.185	4.21	4.34	1.66	6.89	0.11
0.931	0.040	0.029	1209.8	1448.0	1.229	3.95	4.19	1.76	6.53	0.11

RESULTS AND DISCUSSION

The experimentally determined values of the density (ρ), ultrasonic velocity (U), and viscosity (η), isentropic compressibility (K_s), intermolecular free length (L_f), acoustic impedance (Z) molar volume (V_m) and free volume (V_f) for the ternary liquid systems at 298.15 K – 313.15K are reported in **Table 1** and the excess properties, such as ΔK_s, ΔL_f, ΔZ, ΔV_m, ΔU, ΔV_f and $\Delta\eta$ are described graphically in **Figures 1-7**.

In the present investigation, the ultrasonic velocity measurement is used to access molecular interaction between DMSO with Benzene in m-xylene. **Table -1** shows that the values of density (ρ), viscosity (η), and ultrasonic velocity (U), increase with increase in mole fraction of DMSOand decrease with increase in temperature. The pronounced increase or decrease in these parameters with composition of mixtures indicates the presence of interactions between the component molecules in the ternary mixtures. Further, the increase in the number of particles in solution is responsible for increasing the cohesive force between the liquid layers, thereby increasing the co-efficient of viscosity in all systems.

As ultrasonic velocity (U) increases with increase in concentration of DMSO, the isentropic compressibility (K_s), and intermolecular free length (L_f) show reverse trend. The decrease in isentropic compressibility and intermolecular free length with increase in concentration of DMSO shows the considerable molecular interaction between the ternary mixtures, forming hydrogen bonding through dipole- dipole interaction.

The intermolecular free length is the distance covered by a sound wave between the surfaces of the neighboring molecules and it depends upon the intermolecular attractive and repulsive forces. The variation of ultrasonic velocity in a mixture depends upon the increase or decrease of intermolecular free length[13]. Based upon the model for sound propagation, Eyring and Kincaid have proposed that free length is the dominant factor in determining the variation of ultrasonic velocity of the solution[14]. The increase in the value of intermolecular free length with temperature implies that the mean distance between the molecules increases thereby decreasing the potential energy of interaction between them, thus leading to the decrease in the values of velocity and density[15]. The decrease in density with temperature is mainly due to decrease of intermolecular forces because of thermal agitation[16]. The decrease in ultrasonic velocity with increase in temperature indicates the presence of weak interactions between the components of the mixture[17]. A continuous decrease in K_s, L_f and increase of acoustic impedance Z with concentration, at the experimental temperatures, are the clear evidence for the existence of strong interactions like dipole-dipole, and dipole-induced dipole interaction[18]because of the fact that, a polar solvent DMSO is mixed with non-polar solvents like benzene and m-xylene. Mixing of benzene and m-xylene with DMSO tends to break DMSO-DMSO dipolar association releasing overall DMSO dipoles. Consequently the free dipoles of DMSO cause induce dipole moments in the neighboring molecules, benzene and m-xylene, resulting in dipolar-induced dipole interaction leading to contraction in the volume. This is due to the isentropic compressibility (K_s), and intermolecular free length (L_f) decreases with increase in the concentration of DMSO. Again, Table- 1 shows that, the value of free volume V_f, which reflects the close packing of the solvent molecules, decreases with the increase in mole fraction of DMSO.

Through, all the measured parameters indicate the existence of molecular interaction; probably the excess parameters rather offer better confirmation in

understanding the nature of molecular interactions in liquid mixtures.

According to Rajgopal and Chenthilnath[19], the negative values of excess isentropic compressibility (ΔK_S) and excess free length (ΔL_f) in the liquid mixtures are an indication of stronger molecular interaction between the component molecules forming hydrogen bonds through dipole induced dipole type as well as an interstitial accommodation of molecules making the structure more compact, which is shown in **Figure 1**. Similarly, according to Kannappan[20] et al, the negative values of ΔL_f indicates that the sound waves cover long distances due to decrease in intermolecular free length describing the dominant nature of hydrogen bond interaction between unlike molecules in **Figure 2**.

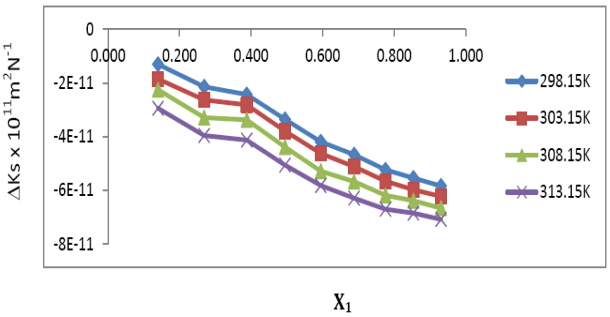

Figure 1: Deviation in isentropic compressibility (ΔKs) vs. mole fraction (x1) of DMSO

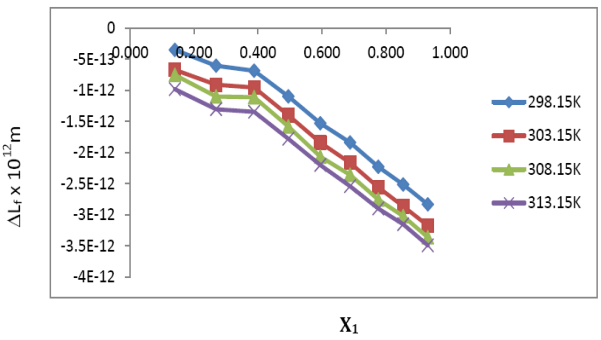

Figure 2: Deviation in intermolecular free length (ΔLf) vs. mole fraction (x_1) of DMSO

The values of excess acoustic impedance (ΔZ) in **Figure 3** are positive, but at 298.15K and 313.15K, initially, at 0.140, 0.269 and 0.388 mole fraction it is negative. The positive excess values of ΔZ clearly suggest that, there exist strong molecular interactions between the components of the ternary liquid mixtures.

The results for the excess ultrasonic velocity (ΔU) plotted in **Figure 4** are positive for the ternary mixtures at all the temperatures studied. The positive values of ΔU increase with the increase in the temperature which indicates the strength of interaction. The deviation in ultrasonic velocity may be explained in terms of relative molecular interaction. So the positive deviation in ΔU suggests the presence of strong interaction between the component molecules.

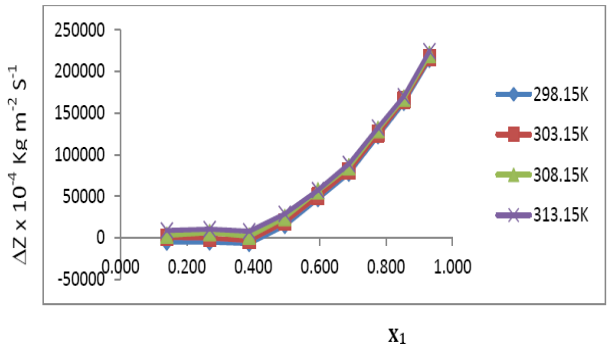

Figure 3: Deviation in acoustic impedance (ΔZ) vs. mole fraction (x_1) of DMSO

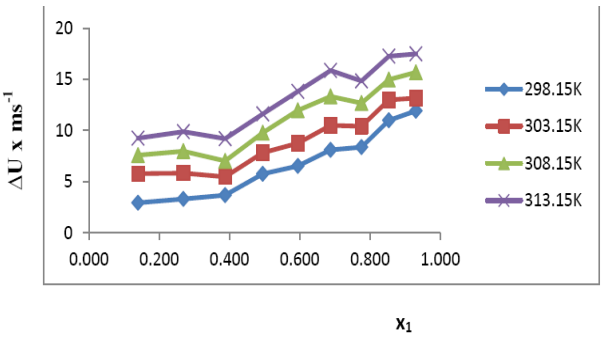

Figure 4: Deviation in Ultrasonic velocity (ΔU) vs. mole fraction (x_1) of DMSO

Figure 5 shows, the variation of ΔV_m with x_1 for the studied ternary systems. The values of ΔV_m were found to be negative over the entire range of compositions. The observed negative ΔV_m values suggest the presence of significant donor-acceptor interactions between the components in the mixtures.

DMSO with its dipole moment (μ=3.96) behaves as a polar liquid with dipole dipole interactions when DMSO is mixed with two non polar hydrocarbons, benzene and m-xylene, either some of the bonds present in the pure component are broken and new bonds are formed. These effects mainly contribute to the sign and magnitude of $\Delta V_{m.}$.

The negative sign of ΔV_f **Figure 6** may be attributed to the dispersive forces in addition to dipole-induced dipole type of interaction operative in the liquid mixtures. The addition of non-polar solvents like benzene and m-xylene to DMSO may lead to depolymerisation of DMSO by breaking intermolecular hydrogen bonds. The negative values of ΔV_f indicate strong molecular interaction[21] suggesting that the mixtures have a tendency for close packing and there is a decrease in free volume in higher mole fraction of DMSO.

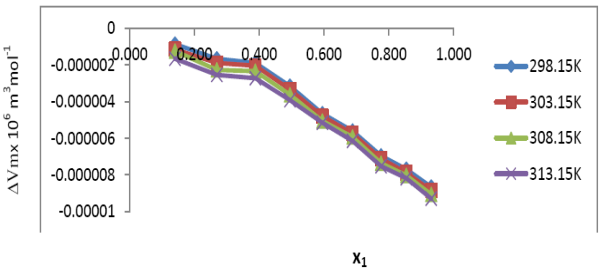

Figure 5: Deviation in molar volume (ΔVm) vs. mole fraction (x_1) of DMSO

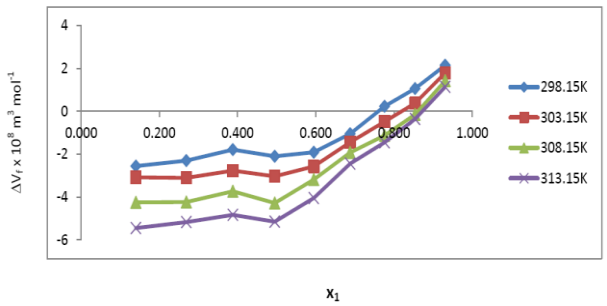

Figure 6: Deviation in free volume (ΔV_f) vs. mole fraction (x_1) of DMSO

The deviation in viscosity ($\Delta\eta$) Figure **7** is found to be negative in the ternary mixtures. The negative values indicate weak dipole-dipole forces because of dispersion forces[22] operating between the component molecules. Negative deviation in $\Delta\eta$ is observed may be attributed to the difference in molecular size of the component molecules[23] in the present mixture.

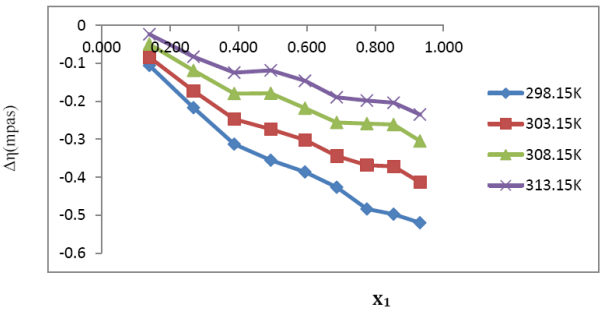

Figure 7: Deviation in viscosity ($\Delta\eta$) vs. mole fraction (x_1) of DMSO

CONCLUSION

Density, viscosity and ultrasonic velocity for the ternary mixtures DMSO, benzene and m-xylene have been reported at 298.15, 303.15K, 308.15K and 313.15K. The addition of non-polar molecules, benzene and m-xylene to the polar DMSO results in breaking of DMSO multimers, thereby releasing several dipoles which may interact with the induced dipoles of non-polar molecules. This causes the negative values of ΔKs and ΔV_f.

The negative sign of ΔKs and ΔVf indicates the presence of strong dipole-induced dipole type of interaction leading to interstitial accommodation through solute-solvent interaction and dispersion forces between the component molecules in the ternary system.

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