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Ultrasonic and Viscometric Studies of Molecular Interaction in Binary Liquid Mixtures of Propylene Glycol and Dimethyl Sulphoxide at Various Temperatures

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Abstract

Ultrasonic studies are extensively used in the confirmation analysis of organic molecules. The binary liquid mixtures play a major role in understanding the nature and strength of molecular interaction. The thermo physical properties such as density (ρ), viscosity (η), and velocity (U) of binary liquid mixtures of Propylene glycol with Dimethyl sulphoxide were determined experimentally over the entire composition range at 303.15K, 308.15K, and 313.15K. From the experimental data the thermo acoustic parameters such as adiabatic compressibility (β_a), intermolecular free length(L_f), acoustic impedance(Z),free volume(V_f),relaxation time(τ), Gibb's free energy(ΔG), internal pressure (π_i), molar sound velocity (R), interaction parameter (χ), were calculated, which are more useful to predict and confirm the molecular interaction present in the binary liquid mixtures.

Keywords: Propylene Glycol, Ultrasonic velocity, intermolecular free length, adiabatic compressibility, interaction parameter, molar sound velocity, internal pressure.

Introduction

The essential frame work of manufacturing material is composed of the scientific and practical interpolation at play among the structure, structural properties and performance of all classes of materials that are potentially useful to the society (1). Even after manufacturing the materials, it is important that one has to analyze its physical and chemical properties. One such property can be investigated by exposing the liquid and solid materials to ultrasonic sound vibrations. Liquid-Liquid mixtures and solutions have found wide application in medical, pharmaceutical, chemical, solvent and related industries. Ultrasonic study of liquids and liquid mixtures has gained much importance in recent years in understanding the nature of molecular interactions in pure liquids and liquid mixtures .Ultrasonic velocity measurements are widely used to study the physical and chemical behavior of liquid mixtures (2-4).

Propylene glycol, also calledpropane-1,2-diol, is a synthetic organic compound with the chemical formula $C_3H_8O_2$. It is a viscous colourless liquid which is nearly odorless but possesses a faintly sweet taste. Chemically it is classed as a diol and is miscible with a broad range of solvents, including water, acetone, and chloroform. It is produced on a large scale and is primarily used in the production of polymers, but also seeks use in food processing, and as a process fluid in low temperature heat exchange applications. Dimethyl sulfoxide (DMSO) is an organosulfur compound with the formula

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$(CH_3)_2SO$. This colorless liquid is an important polar aprotic solvent that dissolves both polar and nonpolar compounds and is miscible in a wide range of organic solvents as well as water. It has a relatively high melting point.

In the investigation, we presented the values of ultrasonic velocity, density and viscosity and evaluated their related thermo acoustical parameters for the binary system of Prpoylene Glycol + Dimethyl Sulphoxide at 303.15K, 308.15K & 313.15K. The results are explained and discussed in terms of molecular interactions present in the binary mixtures.

Experimental

The binary mixtures were prepared by mass, by mixing the calculated volumes of liquid components in airtight glass bottles. In all the measurements, INSREF thermostat with a constant digital temperature display accurate to ±0.01K was used. For all the mixtures and pure solvent triplicate measurements were performed and the average of all values were considered in the calculation. The mass measurements (±0.0001g) were made using an electronic balance. The accuracy of density measurements was 0.0001g.cm^3. A set of 11 compositions were prepared for binary mixtures respectively and also their physical properties were measured. Viscosity is measured by calibrated Ostwald's Viscometer. The speed of sound was determined using a constant frequency (2MHz) ultrasonic interferometer with an accuracy of ± 0.1 m.s^{-1}.

Theory

The adiabatic compressibility β_a was obtained from sound velocity and density measurements as

$$\beta_a = 1/(u^2\rho) \quad (1)$$

The intermolecular free length was calculated using the formula given by Jacobson et al.

$$L_f = K_J \sqrt{\beta_a} \quad (2)$$

where KJ is Jacobson's constant. K_J is the temperature dependent parameter which varies directly with the square root of the absolute temperature i.e.,

$$K_J \alpha \sqrt{T} \quad (3)$$

The acoustic impedance is given as

$$Z = \rho u, \quad (4)$$

where u is the ultrasonic velocity and ρ the density.

On the basis of the dimensional analysis using the free volume concept, Suryanarayana suggested the expression for the internal pressure as

$$\pi_i = bR_gT\,[K_a\eta/u]^{1/2}\rho^{2/3}/M_{eff}^{7/6} \quad (5)$$

where b is the space packing factor (equal to 2 in the present case), R_g, is the gas constant and T is the temperature in degree Kelvin.

From the Eyring's rate process theory, the Gibb's free energy of activation for the relaxation process ΔG was obtained as

$$\Delta G = KT \ln(KT\tau / h) \quad (6)$$

where k is the Boltzmann's constant, h is the Planck's constant and T is the Absolute temperature.

Molar sound velocity (R) and interaction parameter (χ) have been calculated from the following relations.

$$R = (M/\rho)\, U^{1/3} \quad (7)$$

$$\chi = (U/U_{ideal})^2 - 1 \quad (8)$$

The ideal mixing velocity U_{ideal} is given by

$$U_{ideal} = X_1U_1 + X_2U2$$

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Results and Discussion

Table 1. Density(ρ), viscosity (η), ultrasonic velocity(U) for the binary mixtures of propylene Glycol and Dimethyl Sulphoxide at temperatures 303.15K, 308.15K,&313.15K

S. No	X(i) PG	Y(i) DMSO	ρ x 10^{-3} kgm^{-3}			η x 10^{-3} Nsm^{-2}			Ums^{-1}		
			303.15K	308.15K	313.15K	303.15K	308.15K	313.15K	303.15K	308.15K	313.15K
1	0.0000	1.0000	1.1633	1.0881	1.0842	1.3688	1.3608	1.3038	1455.94	1443.97	1438.74
2	0.1000	0.9000	1.1524	1.0767	1.0748	1.6840	1.6346	1.5546	1469.20	1457.17	1451.17
3	0.2000	0.8000	1.1415	1.0758	1.0663	2.0390	1.8803	1.8567	1483.82	1471.17	1464.12
4	0.3000	0.7000	1.1336	1.0720	1.0649	2.5450	2.3385	2.2361	1497.68	1485.65	1477.58
5	0.4000	0.6000	1.1169	1.0701	1.0635	3.1067	2.7159	2.5193	1511.64	1499.31	1490.34
6	0.5000	0.5000	1.0892	1.0664	1.0550	4.1015	3.5442	3.2195	1525.08	1513.8	1503.84
7	0.6000	0.4000	1.0803	1.0579	1.0521	5.3470	4.3711	4.0710	1539.20	1527.62	1516.68
8	0.7000	0.3000	1.0764	1.0512	1.0446	7.4590	5.5922	5.2068	1553.94	1541.37	1529.32
9	0.8000	0.2000	1.0724	1.0465	1.0389	10.5485	7.2825	6.4956	1567.51	1555.82	1542.84
10	0.9000	0.1000	1.0635	1.0409	1.0333	13.9035	9.8541	8.0321	1581.20	1569.57	1555.52
11	1.0000	0.0000	1.0428	1.0342	1.0223	16.9960	13.6214	10.5058	1595.25	1583.65	1568.26

Table 2. Adiabatic compressibility(β_a), intermolecular free length (L_f), acoustic impedance(Z) for the binary mixtures of propylene Glycol and Dimethyl Sulphoxide at temperatures 303.15K, 308.15K & 313.15K

S. No.	X(i) PG	Y(i) DMSO	β_a x 10^{-10} m^2n^{-1}			L_f x 10^{-10} m			$ZKgm^{-2}$ s^{-1}		
			303.15K	308.15K	313.15K	303.15K	308.15K	313.15K	303.15K	308.15K	313.15K
1	0.0000	1.0000	4.0552	4.4077	4.4558	1.2608	1.3145	1.3216	1.6936	1.5711	1.5598
2	0.1000	0.9000	4.0200	4.3740	4.4181	1.2554	1.3095	1.3160	1.6931	1.5689	1.5597
3	0.2000	0.8000	3.9788	4.2948	4.374	1.2489	1.2975	1.3096	1.6937	1.5826	1.5611
4	0.3000	0.7000	3.9328	4.2264	4.3012	1.2417	1.2872	1.2985	1.6977	1.5926	1.5734
5	0.4000	0.6000	3.9182	4.1571	4.2334	1.2393	1.2766	1.2882	1.6883	1.6044	1.5849
6	0.5000	0.5000	3.9473	4.0920	4.1912	1.2440	1.2665	1.2818	1.6611	1.6143	1.5865
7	0.6000	0.4000	3.9072	4.0506	4.1319	1.2376	1.2601	1.2727	1.6627	1.6160	1.5956
8	0.7000	0.3000	3.8473	4.0040	4.0931	1.2281	1.2529	1.2667	1.6726	1.6202	1.5975
9	0.8000	0.2000	3.7950	3.9476	4.0437	1.2197	1.2440	1.2590	1.6809	1.6281	1.6028
10	0.9000	0.1000	3.7608	3.8996	3.9996	1.2142	1.2364	1.2522	1.6816	1.6378	1.6073
11	1.0000	0.0000	3.7682	3.8554	3.9772	1.2154	1.2294	1.2487	1.6635	1.6337	1.6082

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Table 3. Internal pressure(π_i), molar sound velocity (R), relaxation time (τ) for the binary mixtures of Propylene Glycol and Dimethyl Sulphoxide at temperatures 303.15K, 308.15K& 313.15K

S. No.	X(i) PG	Y(i) DMSO	π_i x 10^{6Pa}			R			$\tau \times 10^{-10}$(s)		
			303.15K	308.15K	313.15K	303.15K	308.15K	313.15K	303.15K	308.15K	313.15K
1	0.0000	1.0000	0.7020	0.6833	0.6793	0.7395	0.7884	0.7903	0.7401	0.7997	0.7745
2	0.1000	0.9000	0.7726	0.7426	0.7366	0.7487	0.7992	0.7995	0.9026	0.9533	0.9157
3	0.2000	0.8000	0.8432	0.7946	0.7996	0.7584	0.8024	0.8083	1.081	1.0767	1.0830
4	0.3000	0.7000	0.9362	0.8825	0.8755	0.7660	0.8079	0.8118	1.3345	1.3178	1.2823
5	0.4000	0.6000	1.0226	0.9485	0.9273	0.7799	0.8118	0.8152	1.6230	1.5053	1.4220
6	0.5000	0.5000	1.1540	1.0791	1.0412	0.8021	0.8172	0.8242	2.1586	1.9337	1.7991
7	0.6000	0.4000	1.3084	1.1903	1.1673	0.8112	0.8263	0.8289	2.7855	2.3607	2.2428
8	0.7000	0.3000	1.5391	1.3388	1.3125	0.8167	0.8340	0.8371	3.8262	2.9855	2.8416
9	0.8000	0.2000	1.8235	1.5209	1.4587	0.8221	0.8404	0.8442	5.3376	3.8332	3.5022
10	0.9000	0.1000	2.0793	1.7606	1.6147	0.8314	0.8474	0.8511	6.9719	5.1237	4.2834
11	1.0000	0.0000	2.2661	2.0583	1.8318	0.8504	0.8554	0.8626	8.5393	7.0022	5.5712

Table 4. Free volume (V_f), Gibb's free energy (ΔG), interaction parameter (χ) for the binary mixtures of Propylene Glycol and Dimethyl Sulphoxide at temperatures 303.15K, 308.15K & 313.15K

S. No	X(i) PG	Y(i) DMSO	V_f x 10^{-3} m^3			(-ΔG) x10^{-21}KJ/mole			χ		
			303.15K	308.15K	313.15K	303.15K	308.15K	313.15K	303.15K	308.15K	313.15K
1	0.0000	1.0000	8.5559	8.6252	9.0410	3.8519	3.9095	3.9740	0.0166	0.0254	0.0531
2	0.1000	0.9000	6.3309	6.5389	7.0066	3.8394	3.8982	3.9631	0.0155	0.0239	0.0502
3	0.2000	0.8000	4.8039	5.3555	5.4187	3.8280	3.8904	3.9521	0.0162	0.0236	0.0481
4	0.3000	0.7000	3.4796	3.9030	4.1402	3.8147	3.8775	3.9411	0.0159	0.0239	0.0467
5	0.4000	0.6000	2.6058	3.1491	3.4932	3.8024	3.8689	3.9344	0.0157	0.0231	0.0445
6	0.5000	0.5000	1.7339	2.1346	2.4412	3.7844	3.8529	3.9191	0.0149	0.0235	0.0432
7	0.6000	0.4000	1.1763	1.5736	1.7320	3.7683	3.8401	3.9047	0.0150	0.0229	0.0411
8	0.7000	0.3000	0.7213	1.0978	1.2076	3.7483	3.8250	3.8893	0.0158	0.0223	0.0388
9	0.8000	0.2000	0.4328	0.7461	0.8747	3.7273	3.8090	3.8756	0.0152	0.0226	0.0377
10	0.9000	0.1000	0.2886	0.4784	0.6414	3.7104	3.7903	3.8625	0.0147	0.0220	0.0355
11	1.0000	0.0000	0.2155	0.2971	0.4323	3.6976	3.7703	3.8454	0.0147	0.0218	0.0334

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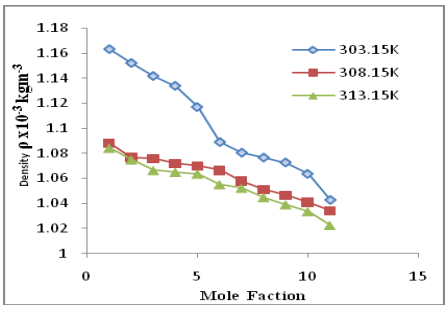

Figure 1. Variation of Density with Mole Fraction

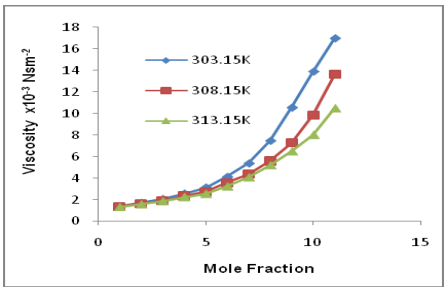

Figure 2. Variation of Viscosity with Mole Fraction

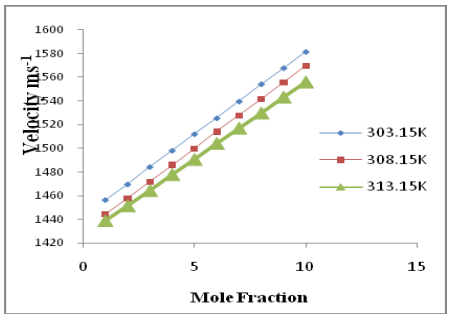

Figure 3. Variation of Velocity with Mole Fraction

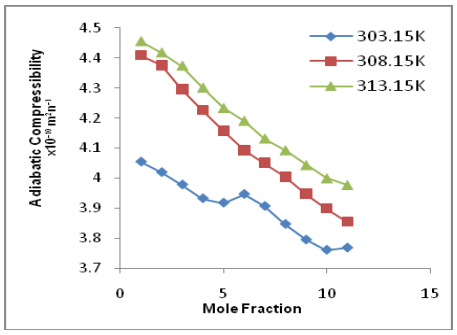

Figure 4. Variation of adiabatic Compressibility with Mole Fraction

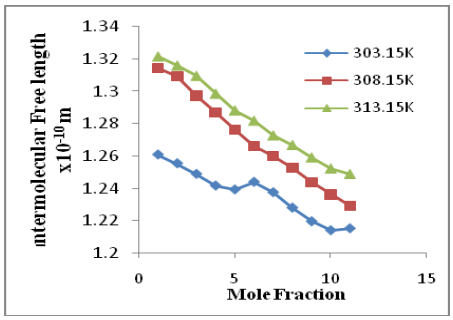

Figure 5. Variation of Intermolecular free length with Mole Fraction

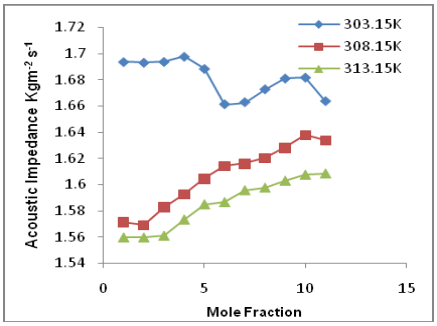

Figure 6. Variation of Acoustic impedance with Mole Fraction

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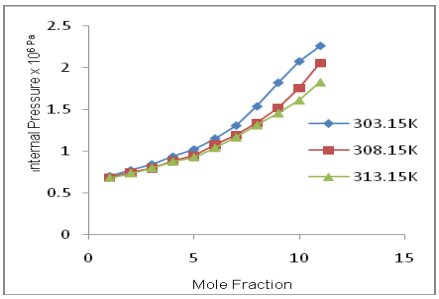

Figure 7. Variation of Internal pressure with MoleFraction

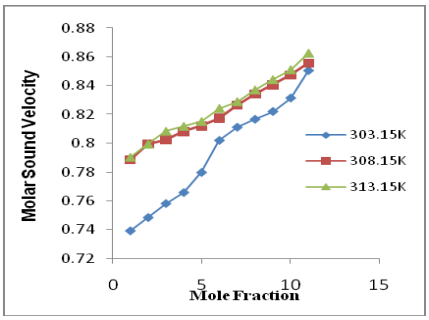

Figure 8. Variation of Molar sound velocity with Mole Fraction

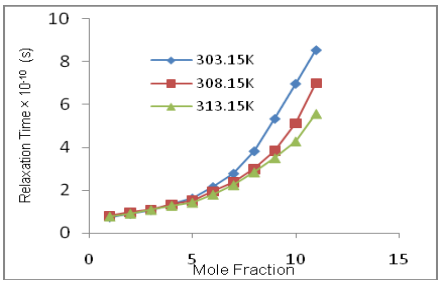

Figure 9. Variation of Relaxation Timewith Mole Fraction

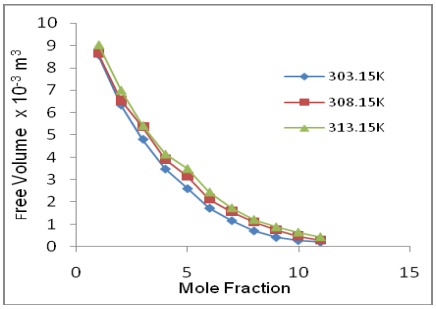

Figure 10. Variation of Free volumewith Mole Fraction

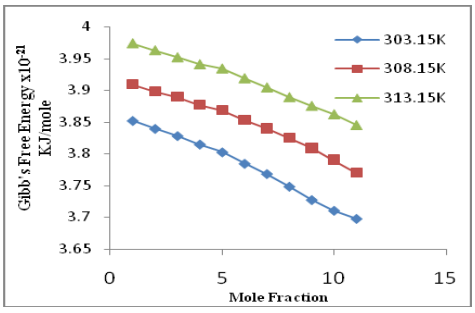

Figure 11. Variation of Gibb's Free Energywith Mole Fraction

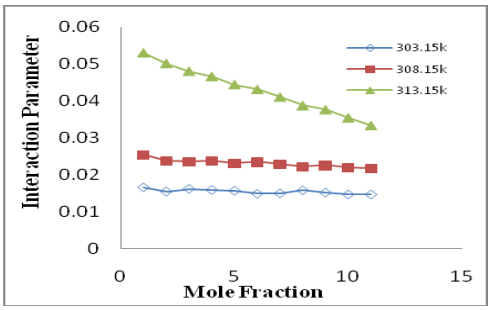

Figure 12. Variation of Interaction parameterwith Mole Fraction

Density, viscosity and ultrasonic velocity of binary mixtures of PG with DMSO are determined experimentally at temperatures 303.15K, 308.15K and 313.15K over the entire mole fraction range and the values are given in Table 1. The values for derived thermo acoustic parameters are computed and are reported in Table 2, 3 and 4 for all the liquid mixtures at the experimental temperatures.

The variation of deviations in density, viscosity and velocity ; thermo acoustic properties like adiabatic compressibility (β_a), intermolecular free length (L_f), acoustic impedance (Z), free volume (V_f), relaxation time (τ), Gibb's free energy (ΔG), internal pressure (π_i), molar sound velocity (R), interaction parameter(χ) as a function of mole fraction at different temperatures are shown in Figure 1-12.

It is observed that density is found to decrease with increase in concentration and decrease with increase in temperature. The decrease in density with mole fraction is due to the shrinkage in volume which in turn is due to presence of solvent molecules. The viscosity is an important parameter in understanding

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the structure as well as molecular interaction occurring in the solutions. Viscosity of solution increases with increase in mole fraction suggest that the extent of complexion increase and more association between solute and solvent molecules. As the temperature increases the cohesion and frictional forces have been diminished due to thermal motion of molecules and relative velocity increases and hence viscosity is found to decrease with increase in temperature. Ultrasonic velocity increase with increase in mole fraction, this behavior shows a moderate strong electrolytic nature in which the solute tend to attract the solvent molecules. Molecular interaction is thus responsible for the observed increase in velocity in these mixtures.

From Table 2, the decrease in adiabatic compressibility (β_a) with increase in mole fraction of Propylene glycol indicates closed packing and increased ionic repulsion. At higher temperature 313.15K, rise in thermal energy causes increase in kinetic energy and volume expansion of the system which results in a increase in adiabatic compressibility. The ultrasonic velocity increases with decrease in intermolecular free length in binary liquid mixture. Therefore, intermolecular free length (L_f) is one of the predominating factor for deciding the nature of variation in ultrasonic parameters in the liquid mixture. In the present study the decrease in intermolecular free length causes increase in ultrasonic velocity, decrease in adiabatic compressibility. Acoustic impedance (Z) is the opposition offered by the medium for the propagation of sound energy. The acoustic impedance decreases with increasing mole fraction of Propylene glycol with DMSO, indicates that significant interaction between the component molecules.

In the study of liquid mixtures, the variation of internal pressure may give some suitable information regarding the nature and strength of forces existing between molecules. It is found that internal pressure (π_i) increases with increase in mole fraction shows that the extent of complex formation. However, the degree of complex formation decreases with increase in temperature.

The molar sound velocity(R) indicates the cube root of sound velocity through one molar volume of solutions called as Rao's constant. The increasing trend of molar sound velocity indicates the availability of more number of components in a given region thus leads to a tight packing of the medium and thereby increase the concentration. Relaxation time (τ) depends on viscosity and adiabatic compressibility of Propylene glycol+ DMSO mixture. From this the time increases with increases in concentration of Propylene glycol +DMSO.

From Table 4, it is observed that free volume (V_f) of liquid mixtures is found to decrease with increase in concentration and increase with increase in temperature. The decrease in free volume may be due to strong association between binary mixtures. The Gibb's free energy (ΔG), decreases with increase in concentration indicating the need for longer time for the co-operative process or the rearrangement of molecules in the mixtures. The Gibb's free energy of activation flow in the mixtures can be obtained on the basis of Eyring rate process theory. These values confirm the availability of intermolecular interactions. The values of interaction parameter (χ) are positive for all the temperatures. This indicates the existence of strong interactions in the binary mixtures.

Conclusion

Ultrasonic studies have been carried out in the solutions of Propylene glycol with DMSO at different temperatures. The study of solution properties of liquid mixtures consisting of organic as well as organosulfur compound finds applications in industrial and technological process. On the basis of experimental values of density, viscosity, ultrasonic velocity and related thermo acoustic parameters for the binary mixtures are calculated. It is concluded that there exists molecular association and molecular interaction between components in the binary mixtures of Propylene Glycol and Dimethyl sulphoxide. The temperature variation indicates that the strength of intermolecular interaction decreases with increase in temperature.

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