Thermodynamic Study of Physicochemical Behaviour in Binary Liquid Mixture of Dimethyl carbonyl and DMSO at Temp = 298 K

Dhavneet Saini
Extension Lecturer, Deptt. Of Chemistry, Govt. College Narnaul, Haryana, India

Abstract: *Intermolecular Free Length, L_f , and available volume, V_a , have been calculated from FLT, CFT and thermo acoustic approach. Density (ρ), ultrasonic speed (u) and excess molar volume (V_m^E) of binary liquid mixture of Dimethyl Carbonyl+ DMSO have been carried out over the different range of composition at 298 K. Thermodynamic parameters like isentropic compressibility K_s , interaction parameter, χ_{12} , Flory parameters, coefficients, A_i and standard deviations, σ (Y^E) have been computed from experimental findings. The excess thermodynamic functions have been fitted to the Redlich-Kister polynomial equation. The experimental ultrasonic speeds have been analyzed in terms of Jacobson Free Length Theory (FLT), Schaaff's Collision Factor Theory (CFT), Nomoto's relation, and Van Dael's ideal mixture relation.*

Key Words: *Ultrasonic Speed, Excess Molar Volume, Schaaff's Collision Factor Theory, Acetone and DMSO.*

1. INTRODUCTION:

The thermodynamic and acoustic properties are very essential for understanding the physicochemical behaviour of the binary and multi-component liquid mixtures. Excess properties of liquid systems, such as molar volumes, are required for testing the theories of solutions, development of separation techniques and equipment, and for other industrial applications. DMSO is an important polar solvent. It is less toxic than other members of this class such as dimethylformamide, dimethylacetamide, *N*-methyl-2-pyrrolidone, and hexa methyl phosphor amide. Because of its excellent solvating power, DMSO is frequently used as a solvent for chemical reactions involving salts. Thus, a study of physical properties data on the binary mixture containing DMSO has attracted considerable interest in the literature. Thus, Dimethyl Carbonyl in DMSO mixed solvent would enable us to have a large number of solvents with appropriate physico-chemical properties, which can be used for a particular chemical process. Moreover, literature survey indicates that no ultrasonic study on this binary system has been reported at 298 K. Therefore, present study was undertaken in order to have deeper understanding of the intermolecular interaction between the components of the above binary liquid mixture. Thus, a study of thermodynamic properties data on the binary mixture of Dimethyl Carbonyl in DMSO has attracted considerable interest in our present study. Research workers in the past have shown that NMR, IR and Raman spectra, have been used to study molecular interactions. The velocity measurement of the propagation of ultrasonic waves and their absorption has already been found to be useful in the study of molecular interactions for inorganic, organic and organo-metallic binary systems. Likewise, researchers have also employed ultrasonic measurements to look into the important consequences of ion-solvent interactions for the structure of electrolytic solutions. References related to the field of medicine, whereas references based on studies on emulsions micro emulsions, polymer surfactants interactions and ultrasonic destruction of surfactants are only a few cases to suggest versatility of the technique.

2. REVIER OF LITERATURE:

In the literature of physical chemistry, the thermodynamic properties of liquids and liquid mixtures constitute an important area of research. The study of liquids and liquid mixtures has been exhaustive since the pioneering work of Vander Waal`s around 1887, who suggested that the shape of the liquid molecules determine the intermolecular interactions. The first few issues of the "Zeitschrift Fur PhysikalischeChemie" 90 years ago devoted large fractions of their pages to the experimental and theoretical studies on the equilibrium properties of liquid mixtures. Since then, numerous research articles dealing with such studies have been published. This publication covered in textbooks, reviews and monographs.

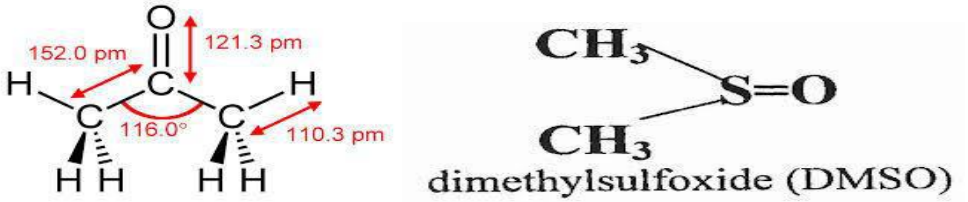

Figure 1.Molecular structure of Dimethyl Carbonyl and DMSO

3.MATERIAL AND METHOD:-

Table 1 Values of Parameters A_j of the Redlich-Kister polynomial equation and corresponding standard deviations, $\sigma(k_s^E)$ for the binary liquid mixture at 298 K.

A_0	A_1	A_2	A_3	$\sigma\,(k_s^E)\,(T\,Pa^{-1})$
	DMSO + Dimethyl Carbonyl			
77.5	-33.20	9.00	-11.90	0.13

DMSO was procured from Fischer Scientific Ltd. and was further purified by the methods given in Vogel text book of practical organic chemistry. Prior to the experimental measurements, both the organic liquids were stored in dark bottles over 0.4 nm molecular sieves to reduce water content and were partially degassed with a vacuum pump under nitrogen atmosphere. The purities of all the samples determined by chromatographic analysis were better than 0.996 on a molar basis. Binary mixtures are prepared by mixing appropriate volumes of the liquid component in the specially designed glass bottles with air tight Teflon coated caps. The thermodynamic properties are measured on the same day immediately after preparing each composition. The uncertainty in mole fraction is ±0.0001. A multi frequency digital micrometer reading ultrasonic interferometer (M-81, Mittal Enterprises, New Delhi) operating at 1, 2, 3 and 4 MHz was used to measure the ultrasonic velocity of the Binary liquid mixtures (with an uncertainty of ± 0.3%) at a constant temperature of 298 K by using a digital constant temperature water bath. The temperature stability is maintained within ± 0.001 K by circulating thermo stated water around the cell with a circulating pump. In order to minimize the uncertainty of the measurement, several maxima are allowed to pass and their number (fifty) is counted. All maxima are recorded with the highest swing of the needle on the micrometer scale. The total distance, d (cm) moved by the reflector is given by $_{d=}n\lambda/2$ whereλ is the Wavelength. The frequency,v , of the crystal being accurately known (2.0 MHz), the speed of sound, u , in ms^{-1} is calculated by using the relation $u = \lambda v$. Excess molar Volume,V_m^E , was calculated by specially designed double limbed glass dilatometer fitted with a micro capillary (± 0.01 cm) in the centre. The density of solutions was measured by a double arm pyknometer of 10 ml bulb capacity and a Capillary of an internal diameter of about 1.0 mm. The mark of the stem was calibrated by double distilled water (conductivity less than 1×10^{-6} ohm^{-1} cm^{-1}) with 0.9970 and 0.9940 g cm^{-3} as its density at 298.15 K and 308.15 K, respectively and Dimethyl Carbonyl with buoyancy corrected. The accuracy of the density results was ± 0.0001 (g cm^{-3}). Before each series of measurements, the instrument was calibrated with triple distilled freshly degassed water. The accuracy of the density results was ± 0.00001 (g/cm^3). Weight measurement were performed on a Mettler Toledo AB 135-S/FACT, single pan analytical balance, with a precision of 0.01 mg. The densities, and ultrasonic velocities, u , of the pure liquids were in good agreement with the values found in the literature and are presented in Table 1

5. RESULT:

Density (ρ), ultrasonic speed (u) and molar excess volume (V_m^E) of binary liquid mixture of Dimethyl Carbonyl + DMSO have been observed over the entire range of composition and at 298 K. From these experimental results, parameters such as deviation in isentropic compressibility, ΔK_s , interaction parameter, χ_{12} , Flory parameters, Coefficients A_i , standard deviations σ (Y^E) and molar sound velocity, R_m , have been estimated. The excess functions have been fitted to the Redlich-Kister polynomial equation. The experimental ultrasonic velocities have been analyzed in terms of Nomoto's relation, Van Dael's ideal mixture relation, Jacobson Free Length theory and Schaaff's Collision Factor theory. Intermolecular Free Length, L_f , and availablevolume,V_a , have been calculated from Jacobson Free Length theory, Schaaff`s Collision Factor theory, and Thermo acoustic Approach for binary liquid system of Dimethyl Carbonyl + DMSO at 298 K. The observed negative values of ΔK_s and excess molar volume V_m^E and positive values of Δu for these mixtures imply that the specific chemical dipole-dipole interactions between unlike molecules dominate over the physical dispersive interaction and dipole-dipole interaction between like molecules.

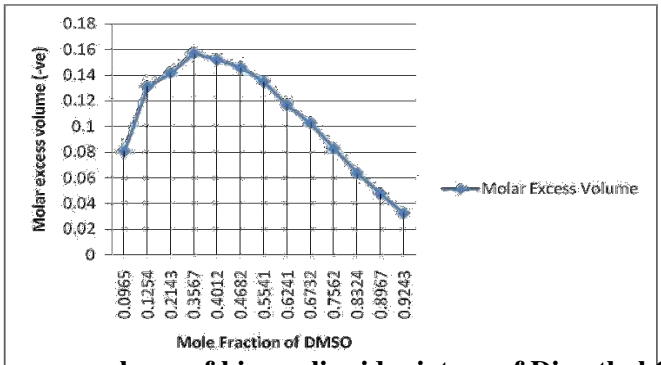

Figure 2- Molar excess volume of binary liquid mixture of Dimethyl Carbonyl in DMSO.

Table 2.Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's and Van Dael and Vangeel's idealmixing relation and percentage error in calculated values for Dimethyl Carbonyl + DMSO.

x_1 DMSO	u (m/s)				% error			
	FLT	CFT	NOM	VD	FLT	CFT	NOM	VD
0.0000	1147.0	1147.0	1147.0	1147.0	0.00	0.00	0.00	0.00
0.1150	1171.6	1173.9		1173.2	2.28	0.48	0.12	0.09
0.2262	1190.3	1193.3	1194.1	1194.4	4.48	0.82	0.10	0.55
0.3338	1220.0	1225.4		1226.0	5.30	0.93	0.06	0.00
0.4380	1249.6	1254.9	1254.0	1254.2	5.76	0.86	0.00	0.08
0.5390	1288.8	1294.3		1294.0	6.04	0.80	0.10	0.18
0.6369	1310.3	1313.4	1315.3	1315.6	5.91	0.71	0.15	0.23
0.7371	1330.8	1334.9	1334.4	1334.5	4.86	0.41	0.19	0.24
0.8238	1371.1	1375.8		1375.6	3.79	0.28	0.18	0.22
0.9032	1403.3	1401.4		1401.4	2.57	0.19	0.17	0.19
1.0000	1445.0	1445.0	1445.0	1445.0	0.00	0.00	0.00	0.00

4. CONCULSION:

All the systems of DMSO with Dimethyl Carbonyl shows negative deviation through ΔK_sisotherms over entire range of mole fraction . A clear minima at the mole fraction around $x_1 = 0.3939$, indicates that the maximum interactions are atthat this mole fraction range.it is observed that Δu values are positive while, ΔK_s values are negative, such trends of positivedeviation in a speed of sound and negative deviation in isentropic compressibility is quite common .

In pure DMSO, there is dipole–dipole as well as the usual dispersive interaction. The effect of adding a non polar second component is primarily to disrupt the dipolar interaction of the first component, but when the second component is also polar, the dipole-dipole interaction between unlike molecule is most likely which result in contraction of volume and the mixture becomes the less compressible**.**

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