MOLECULAR INTERACTION STUDIES OF PHENOL WITH ACETALDEHYDE USING ULTRASONIC AND FTIR TECHNIQUE

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ABSTRACT

The densities (ρ), viscosities (η) and ultrasonic velocities (U) were measured for the binary mixtures of Phenol with Acetaldehyde at 303K. Excess volumes (Vm^E), isentropic compressibilities (ks^E) and isentropic compressibilities (ks^E) were determined from these experimental findings. To obtain their coefficients and standard deviations, the excess or deviation properties were based on Redlich-Kister polynomial equation. Depending on the molecular interactions between the components of hetero molecules, the excess or deviation properties were considered either negative, and the nature of liquid mixtures was studied in terms of molecular interactions by steric and electronic effects. The FTIR provides support to thermodynamic studies to classify different interactions between molecules that are unlike them.

Keywords: Binary Liquid, Phenol, Acetaldehyde, Excess Values and FTIR.

1. INTRODUCTION

Thermal properties such as density, viscosity, sound speed (u) and their differences of binary liquid mixture proportions have been used in the design of chemical and biological engineering processes [1] and in the creation of modern theoretical models for engineering applications [2-4]. Excess or variance parameters such as excess molar volume (V^E), variation in istropic compressibility (in some cases) and excess intermolecular free length (in other cases) can be derived from mass, viscosity and sound velocity. Such parameters are efficient in obtaining essential knowledge about molecular interactions between binary and ternary mixtures unlike molecules [5, 6]. The thermodynamic excess parameters are used for practical chemical engineering purposes such as chemical process, chemical separations, mass transfer operations (adsorption, evaporation and precipitation), heat transfer and fluid flow [7]. The Fourier-transform infrared (FTIR) is a method used to identify the classification of the molecule by knowing its functional group. By using FTIR spectroscopy, we can observe [8-15] that hydrogen interaction between molecules takes place and it is a very interesting class of intermolecular interactions.

In the present work, we have revealed the nature of intra and inter molecular interactions between phenol and acetaldehyde molecules in the liquid mixtures with aid of excess thermodynamic properties and Fourier transform infrared spectroscopic (FT-IR) studies. By using the measured densities (ρ) and speeds of sound *(u),* excess volumes (Vm^E), isentropic compressibilities (k_s) and excess isentropic compressibilities (k_s^E) were also determined and details are displayed for these binary mixtures at temperature 303 K. The excess properties is associated with the polynomial equation Redlich-Kister. In comparison, the FT-IR spectrum reported for pure liquids and their mixtures confirms the molecular interactions between component molecules by changing the vibrational frequencies -O-H,-C-H and -C-O stretch.

2. MATERIAL AND METHOD

2.1. Material

The mixtures of phenol and acetaldehyde of various concentrations ranging from 0 M to 0.1M were prepared by taking analytical reagent grade and spectroscopic reagent grade chemicals with minimum assay of 99.9% are procured from E-Merck Ltd (India). The above experimental solutions are of equimolar concentrations of different solutions constituting the system which are under study.

2.2. Experimental details

The ultrasonic velocity measurements of phenol with acetaldehyde solutions was rendered in the 2 MHz (Model F-81 Mittal enterprises, New Delhi) fixed frequency ultrasonic interferometer at 303k tempera-

ture. The density measurements are calculated at 303k temperature using a specific gravity bottle by normal operating practice and the viscosity using Ostwald's viscometer calibrated with double distilled water sensitivity of $\pm$ 0.001 percent. For such measurements the FTIR spectra are obtained utilizing the Fourier Transform Infra Red (FTIR) Spectrometer (Spectrum RX, Perkin Elmer).

2.3. Thermodynamic parameters

2.3.1. Molar Volume of the Binary Liquid Mixture (Vm)

The molar volume of the system at every mole fraction for the mixture is given by

$$V_m = \frac{M_{eff}}{\rho \, mix} \tag{1}$$

Where $M_{eff} = M_1 X_1 + M_2 X_2 /(X_1 + X_2)$

2.3.2. Excess Molar Volume

The difference between the molar volume of the mixture and the sum of the individual molar volume times the mole fraction is defined as excess volume or excess molar volume

$$V_m^E = V_m - (V_{m1} X_1 + V_{m2} X_2) \tag{2}$$

2.3.3. Adiabatic Compressibility (Ks)

Adiabatic compressibility is a function of the interaction or dissociation or repulsion between molecules. Singh and Kalsh proved that the adiabatic compressibility for unassociated and weakly associated molecules would be independent of the temperature and pressure. This also defines how the solvent molecules are arranged around the liquid molecules. The structural arrangement of the molecule affects the adiabatic compressibility. It can be calculated using the equation.

$$ks = \frac{1}{U^2 \rho} \tag{3}$$

Where,

U is the velocity in m/s

ρ is the density in kg/m^3

2.3.4. Excess Isentropic Compressibilities (ks^E)

An ideal mixture of isentropic compressibility is considered to be additive in terms of volume fraction. The difference between the compressibility of a real solution and that of an ideal solution is called excess isentropic compressibility. The values of excess isentropic compressibilities (ks^E) were calculated from the following relations

$$k_s^E = k_s - k_s^{id} \tag{4}$$

3. RESULTS AND DISCUSSION

It is seen that (Table 1) in the present systems of binary liquid mixtures, the viscosity (η) and the ultrasonic velocity (U) and the density (ρ) increases with increasing concentrations of phenol. The variance in ultrasonic velocity in a mixture depends on the increase (or) decrease in intermolecular free length after combining the components on the basis of a pattern, suggested by Eyring and Kincaid [16] for sound propagation.

The mole fraction (X_1), experimental densities (ρ) and calculated excess volume (Vm^E) data are presented in Tables from 1-2 at 303 K. The plots of excess volume (Vm^E) with mole fraction, X_1, for the binary mixtures of Acetaldehyde with phenol 303K are shown. The values are negative in sign in the whole concentration region for phenol with acetaldehyde.

In the present study, phenol and acetaldehyde are self-associated through hydrogen bonding in the pure state due to the presence of electron donor and electron acceptor sites. When the phenol molecules are mixed with acetaldehyde, the disruption of hydrogen-bonded structures present in pure phenol or acetaldehyde acid takes place with subsequent formation of the intermolecular hydrogen bond between component molecules in liquid mixtures. On the other hand, interstitial accommodation of phenol molecules in hydrogen-bonded acetaldehyde aggregates (packing effect) and makes a negative V_m^E.

The measured speed of sound (u), calculated isentropic compressibilities (ks) and excess isentropic compressibilities (ks^E) for the binary mixtures of Phenol with acetaldehyde are report in Table 2 The plots of excess isentropic compressibilities (ks) with mole fraction (X_1), for the binary mixtures of phenol with acetaldehyde at 303K

It is ascribed from Table 2, that, κs^E property is negative for phenol with acetaldehyde in binary liquid mixtures. Figure also reveals that negative κs^E data in the binary mixture of phenol with acetaldehyde indicate that the liquid mixtures have low compressibilities and also show more effective binding than when compared to pure liquids. Furthermore, the negative values for the binary mixtures under study suggest that there are variations in molecular sizes and interstitial accommodation (H-bonding) between binary liquid mixture constituent molecules [17, 18]. It can be inferred that as the frequency of the interaction between the intermolecular forces decreases, the values of κ_s^E are more negative.

The excess property (V_m^E) was fitted by Redlich-Kister type polynomial equation and the calculated values of the polynomial coefficients a_o, a_1, and a_2 along with their standard deviations (σ) are presented in Table 2.

Table 1: The value of density (ρ), viscosity (η), velocity (U) and Molar volumes (Vm), phenol with Acetaldehyde at 303K

Concentration		Density (ρ) Kg/m³)	Viscosity (η) (x10⁻³ NSm⁻³)	Ultrasonic velocity U/(ms⁻¹)	Molar volumes Vₘ (m³/mol)
X_1	X_2				
0	1	877	1.8512	1011	5.02
0.0494	0.9506	884	1.9251	1025	5.26
0.1671	0.8329	910	2.0124	1075	5.76
0.3188	0.6812	925	2.2541	1150	6.49
0.522	0.478	931	2.4512	1200	7.54
0.8082	0.1918	944	2.5142	1230	8.95
1	0	955	2.6543	1311	9.85

Table 2: The value of), Excess Molar volumes (VmE), Adiabatic Compressibility (ks) and Deviation in Adiabatic compressibility (KsE) of phenol with Acetaldehyde at 303K

Concentration		Excess Molar volumes Vₘᴱ (m³/mol)	Adiabatic Compressibility (ks) (N⁻¹m²) ×10⁻¹⁰	Deviation in Adiabatic compressibility (ksᴱ) (N⁻¹m²) ×10⁻¹⁰
X_1	X_2			
0	1	0	11.156	0
0.0494	0.9506	-9.61	10.767	-6.481
0.1671	0.8329	-9.12	9.5091	-7.739
0.3188	0.6812	-8.39	8.1745	-9.074
0.522	0.478	-7.34	7.4591	-9.789
0.8082	0.1918	-5.93	7.0019	-10.25
1	0	0	6.0924	0

Table 3: Coefficients of the Redlich-Kister type polynomial and the corresponding standard deviations σ (VmE)-(ksE) for the binary mixtures Phenol with Acetaldehyde at 303K

Parameters	Temperature(K)	A_0	A_1	A_2	Standard deviations (σ)
Vmᴱ	303K	-38.38	70.14	-28.74	0.2258
KₛE	303K	-26.33	5.34	22.76	0.6145

3.1. FT-IR STUDIES

3.1.1. Stretching region (-OH)

Figures.1-3 confirms the FT-IR spectrum of pure phenol or acetaldehyde and their binary mixtures in the range of 350-4500cm-1 at equimolar composition. In Figs.1-3 we can find a wide band at 3558cm⁻¹ and 3522 cm⁻¹ for pure phenol and phenol at equimolar composition with acetaldehyde, respectively. The -OH stretching level for the binary liquid mixtures of phenol with acetaldehyde at equimolar composition is changed from 3522 cm⁻¹ respectively. It clearly states that, attributed to the presence of acetaldehyde, degradation of the hydrogen bound complexes occurs in phenol molecules.

3.1.2. C=O Stretching region:

The FT-IR spectrum of pure components and their liquid mixtures at a range of 1600-1800 cm⁻¹ equimolar composition are shown in Fig. 1-3. Here in, at 1796 cm⁻¹ a sharp band appears indicating the -C = O stretching acetaldehyde vibration frequency. The absorption rate of the strong C = O strclching band of get changed acetaldehyde was moved from 1796 cm⁻¹ to 1760cm⁻¹ for the binary liquid mixtures at equimolar composition respectively due to the introduction of acetaldehyde to phenol. This behavior is due to the formation of strong intermolecular hydrogen bonding between oxygen atom of carbonyl (C=O) group of acetaldehyde acid and hydrogen atom of -OH group of' phenol molecules (-C=O-----H-O-).
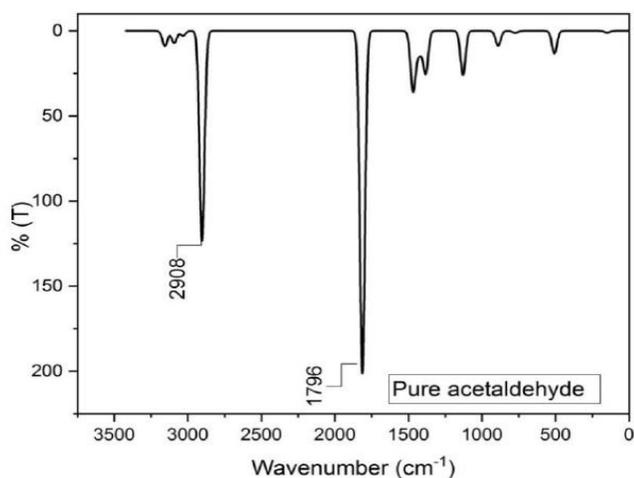
Fig. 1: FT–IR spectrum of Pure Acetaldehyde
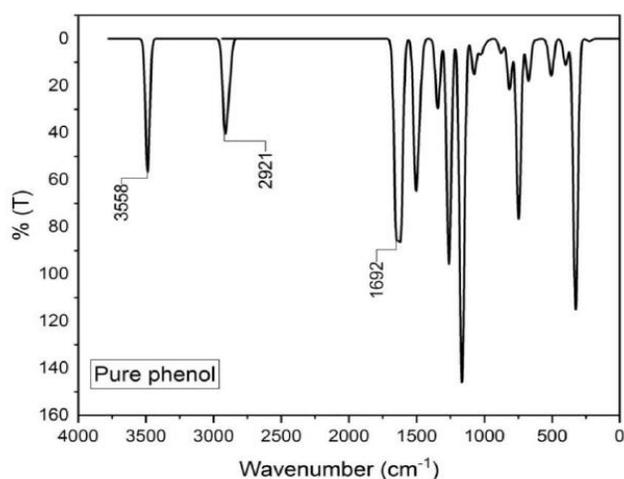
Fig. 2: FT–IR spectrum of Pure Phenol
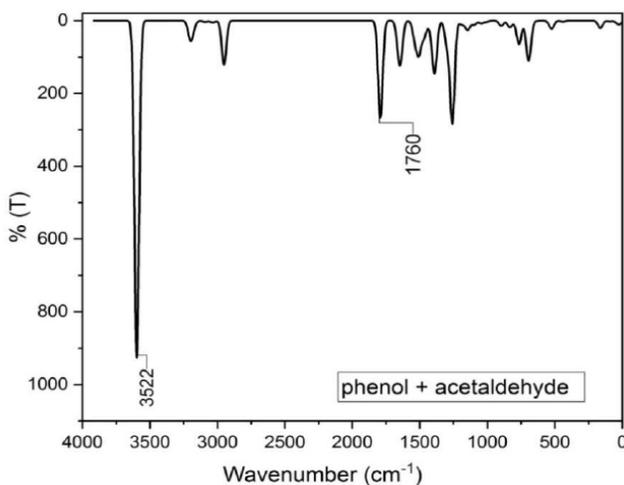
Fig. 3: FT–IR spectrum of Phenol with Acetaldehyde at equimolar mixtures

3.2. Discriminating weak interaction types by filling color to RDG isosurfaces:

The reduced density gradient (RDG) is calculated using Multiwfn.[19] Such RDG is then visualized which makes it easy to recognize the hydrogen bond. By integrating the RDG function with $\Omega(r)$ function, we may differentiate between the form and strength of the weak interaction [20].

$$RDG(r) = \frac{1}{2(3\pi^2)^{\frac{1}{3}}} \frac{[\nabla\rho(r)]}{\rho(r)^{\frac{4}{3}}} \qquad (5)$$

$$\Omega(r) = \sin n\,(\lambda_2(r))\,\rho(r) \qquad (6)$$

Where RDG is the diminished gradient of energy and where $\Omega(r)$ is the overall mass of the electron. According to the principle of atom in molecule (AIM),[21-22] the relationship with the second-largest own value of the Hessian matrix of electron density as seen in Eq. (5). (6). $\rho(r)$ is an essential indicator of weak interaction strength, while the form of weak interaction is defined by the λ_2 function of sine. It is also possible to evaluate the weak interactions of different forms by drawing the scatter graph between function λ_1 (RDG) and function λ_2 ($\Omega(r)$). Figure demonstrates the formula obtained by multiplying the equation of $\rho(r)$ and sine λ_2 and thereby producing the RDG isosurface. 4 (a) with a contour value of 0.5 and an isosurface of the RDG between -0.04 and 0.02. The hydrogen bond increase is situated at -0.036 a.u., which means that the hydrogen bond is particularly high in acetaldehyde-mixed phenol. Similarly, one can distinguish the weak interactions in Fig. 4(b). It can be ascertained directly from Fig. 4 (b) the hydrogen bond between OH ……. O = C is strong.
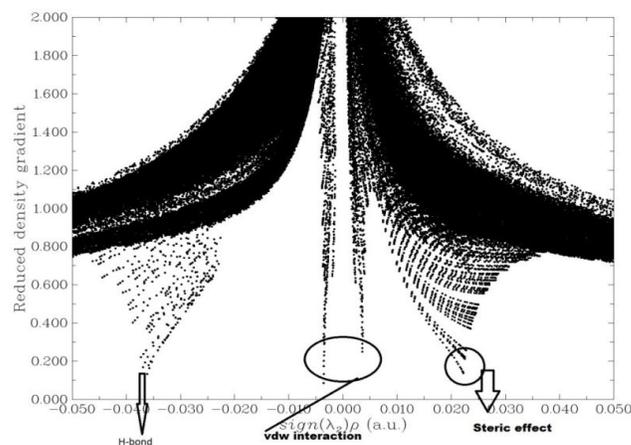
Fig. 4: (a) (Color online) Plot of reduced density gradient (RDG) versus $\Omega(r)$ for function value 1 and function value 2.
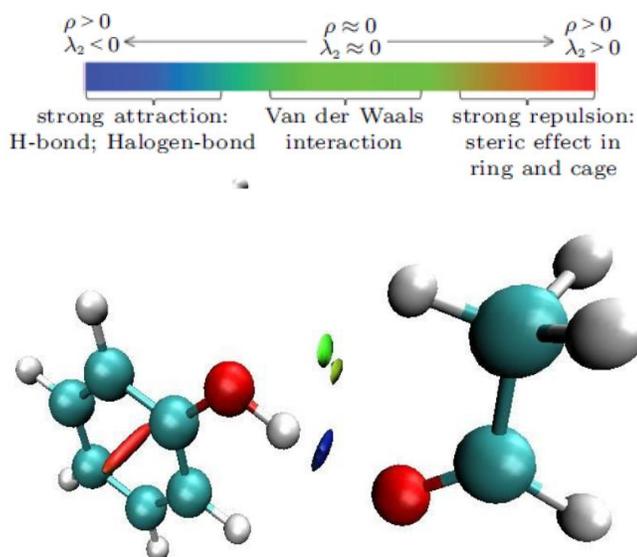
Fig. 4: (b) (Color online) ((b) Different types of weak interactions represented by different color gradients as well as RDG isometric surfaces.

4. CONCLUSION

In the present work, the excess properties (Vm^E and ks^E) were determined for the binary mixtures containing phenol with acetaldehyde. It was observed from the measured data that the excess volume data has inversion sign for the binary mixtures. On the other hand, the excess adiabatic compressibilities exhibited negative behaviour for the binary mixtures of phenol with acetaldehyde. However, these excess properties and FT-IR data indicates the formation of intermolecular hydrogen bonding (-C=O---H-O-) between carbonyl atom of the acetaldehyde and hydroxyl group of phenol by the strong hydrogen bonds in self-associated phenols. Furthermore, these excess properties ((Vm^E and Ks^E) were correlated with Redlich-Kister polynomial equation.

5. REFERENCES

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