# EFFECT OF INTERMOLECULAR INTERACTIONS ON LPG GAS SENSING IN THE THIN FILM OF Zn/$CuCl_2$

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**Abstract**

**The spray technique methods have been employed successfully for the deposition of Cu/CuO impregnated ZnO thin films suitable for sensing LPG gas. The observed change in sensitivity of those films upon exposure to LPG gas in air has been explained on the basis of the electrical properties and synthesised ultrasonic properties. The synthesis of ZnO: CuO/Cu films are employed to study the density and ultrasonic velocity in binary mixture of ethanol (EtOH) + Water have been measured over the 0.6 mol% concentration level at RT using single crystal variable path interferometer working at 2 MHz. Various acoustic parameters such as acoustic impedance (Z) adiabatic compressibility (β) intermolecular free length (L), relative association (R.A.), Molecular volume ($V_m$) and molecular sound velocity ($R_m$) have been calculated. The obtained result have been used to explain the nature and strength of intermolecular interaction prevalent in the liquid and its effect over the sensing activity.**

**Keywords: ZnO, Cu/CuO, acoustics, gas sensor.**

## 1.0 Introduction:

High expletive ultrasonic measurement at single frequency or in limited frequency is often used for liquid characterization in basic research as well as in the broad verity of application. Ultrasonic's is a versatile tool for studying the properties of solids, liquid and liquid crystals. The theory of adsorption and desorption are well established in solids. Ultrasonic adsorption measurements in materials especially solid crystalline phases are important because of its widespread use in environmental and biological application. Accumulation of absorption data and the classification of the possessions of adsorption are therefore desired in various systems. We have made the ultrasonic velocity and density measurement at various concentration of the Zn/$CuCl_2$admixture are used to study the physicochemical behaviour and molecular interaction such as ion-solvent interaction solvent in distilled water, liquid mixture and solution. The nature and the degree of molecular interactions in different solution changes depending upon the nature of solvent, however the structure of the solute molecule and the extent of solution taking place in the mixture solution. As this parameter throw more light on ion -ion and ion -solvent interaction.

LPG is the most useful gas for combustible purpose for domestic as well as industrial application [1-6]. In the recent era the use of LPG is widely expanded and enters in the urban, slums and all sorts of businesses, wherever the heating is required. It is potentially hazardous because of explosion accident might be caused when they leak out by mistake so the detection of LPG in domestic appliances must be identified now a days by investigating highly sensitive gas sensing material which has been discussed in this study.

Zinc oxide (ZnO) is one of the most initially revealed metal oxide gas sensing materials. It is an n-type semiconductor with direct energy wide band gap of about 3.37eV at room temperature. ZnO is used as a semi conducting gases because of their chemical sensitivity to volatile and other reducing gases, their high chemical stability, suitability to doping non-toxicity and low cost. Furthermore ZnO is used as semi conducting gas sensor due to its conductive change when exposed to oxidizing gases.

The Various acoustic parameters such as acoustic impedance (Z) adiabatic compressibility (β) intermolecular free length (L), relative association (R.A.), Molecular volume ($V_m$) and molecular sound velocity ($R_m$) have been calculated and compared with same concentration based thin film used for gas sensing application. Various concentration of modified samples As this parameter throw more light on ion-ion and ion-solvent interaction, an ultrasonic study of $ZnCl_2/CuCl_2$ in ethanol-water mixture has been made at RT and at studied at 2 MHz.

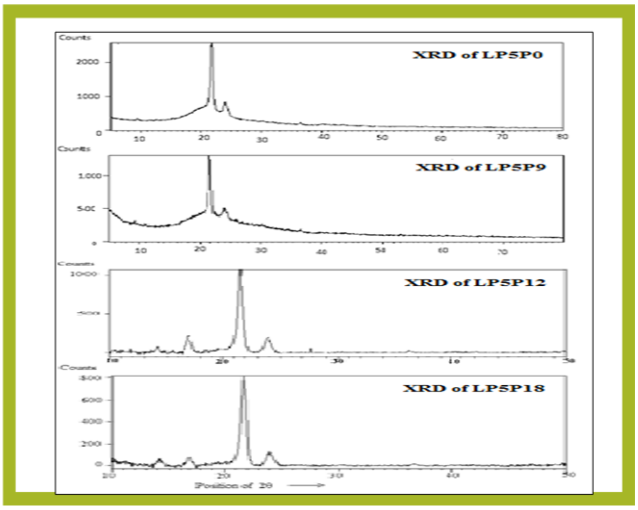
**2.0Experimental**

One mole solution of $ZnCl_2$ and $CuCl_2$was prepared in distilled water to which X wt. % of (X=0.1, 0.2, 0.3, 0.4, 0.5, 0.6 wt %) $CuCl_2$ solutionwas added in $ZnCl_2$ Solution. The mixture of $ZnCl_2/CuCl_2$ (30%) is further added in to 70 % of ethanol used as carrier concentration. The ethanol and complex mixture have been prepared in glass stopper flask by weight method. The ultrasonic velocities in pure solvents as well as various mixtures were measured using ultrasonic interferometer at a constant frequency of 2 MHz. The temperature of the solutions placed in the interferometer cell was maintained at constant 25 ± 1 $^oC$ by circulating water around the cell from a thermostat. The experimental value of density and ultrasonic velocity were used to focus on change in electrical behaviour of the material.

**3.0 Results and Discussion:**

**X-ray Diffraction (XRD)**

X-ray diffraction of samples LP5P0, LP5P9, LP5P12 and LP5P18 were recorded on XPERT-PRO 11023505 SAIF PU, Chandigarh an are shown in Figure (1).



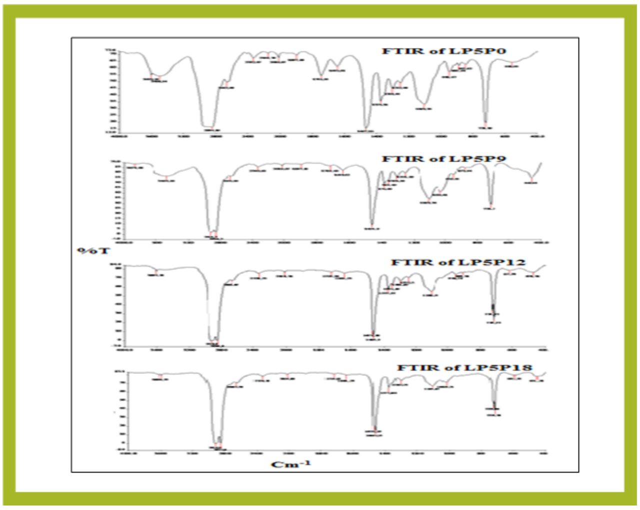




**Figure 1: XRD of LP5P0, LP5P9, LP5P12 and LP5P18 Figure 2: FTIR Spectra of LP5P0, LP5P9, LP5P12 and LP5P18**

XRD [8] diffraction from the (110) and (200) planes are observed in undoped ZnO were centred at 2θ = $21.9^0$ and 2θ = $24.2^0$ corresponding to d-spacing of 4.05 $A^0$ and 3.75 $A^0$ respectively. XRD pattern of LP5P0 shows very sharp, small, prominent peaks at 2θ = $21.79^0$ and 2θ = $24.04^0$ corresponding to d-spacing of 4.07 $A^0$ and 3.70 $A^0$. XRD pattern of LP5P9 shows very sharp, small, prominent peaks at 2θ = $21.68^0$ and 2θ = $23.91^0$ corresponding to d-spacing of 4.09 $A^0$ and 3.72 $A^0$ . XRD pattern of LP5P12 shows very sharp, small, prominent peaks at 2θ = 21.59 $^0$and 2θ = $23.91^0$ corresponding to d-spacing of 4.11 $A^0$ and 3.72 $A^0$ and XRD pattern of LP5P18 shows very sharp, small, prominent peaks at 2θ = $21.91^0$and 2θ = 23.94 $^0$corresponding to d-spacing of 4.06 $A^0$ and 3.72 $A^0$. XRD pattern of LP5P0, LP5P9,LP5P12 and LP5P18 thin films suggest small crystalline phase along with amorphous phases also addition of Cu in ZnO matrix affects the crystallinity.

**Fourier Transform Infrared Spectrometer**

FTIR Spectra of thin film samples LP5P0, LP5P9, LP5P12 and LP5P18 was recorded in wavelength region 400-4000 $cm^{-1}$shown in figure (2)FTIR modelPerkin Elmer Spectrum RX1, RC SAIF PU, Chandigarh.

FTIR spectra of ZnO with 1 % Cu (LP5P0)shows peak at 2844.16 $cm^{-1}$due to asymmetric and symmetric $CH_2$ stretching vibration. The Peak at 1467.15 $cm^{-1}$ and 721.19

$cm^{-1}$corresponds to C-H bending and racking amorphous of $CH_2$ group respectively. The band at about 3498.54 $cm^{-1}$ belongs to O-H stretching vibration. The peaks at 1745.54 $cm^{-1}$ and 1643.61 $cm^{-1}$ are due to C=O stretching of carbonyl group and vinyl group respectively. The spectra of LP5P9shows peaks at 2914.2 $cm^{-1}$ and 2854.2 $cm^{-1}$ are due to asymmetric and symmetric $CH_2$ stretching vibration of LDPE. The Peaks at 1464.9 $cm^{-1}$ and 721.29 $cm^{-1}$correspond toC-H bending and racking amorphous of $CH_2$ group respectively. The band at about 3463.56 $cm^{-1}$ belongs to O-H stretching vibration. The peaks at 1719.66 $cm^{-1}$ and 1641.62 $cm^{-1}$ are due to C=O stretching of carbonyl group and vinyl group. The spectra of LP5P12 shows peaks at 2920.0$cm^{-1}$ and 2848.0 $cm^{-1}$ are due to asymmetric and symmetric $CH_2$ stretching vibration of LDPE. The Peaks at 1463.5 $cm^{-1}$ and 719.23 $cm^{-1}$ correspond to C-H bending and racking amorphous of $CH_2$ group respectively. The peaks at 1719.76 $cm^{-1}$ and 1641.75 $cm^{-1}$ are due to C=O stretching of carbonyl group and vinyl group . The spectra of LP5P18 shows peaks at 2918.0 $cm^{-1}$ and 2853.0 $cm^{-1}$ are due to asymmetric and symmetric $CH_2$ stretching vibration of ZnO. The Peaks at 1463.15 $cm^{-1}$ and 719.38 $cm^{-1}$ correspond to C-H bending and racking amorphous of $CH_2$ group respectively. The peaks at 1719.81 $cm^{-1}$ and 1640.79 $cm^{-1}$ are due to C=O stretching of carbonyl group and vinyl group.

The acoustic impedance (Z), adiabatic compressibility (β), Inter molecular free length (L) relative association (R.A.) and density is calculated and given in table and represented graphically as shown in figure.

It is observed that the density values increase from 0.0 wt% to 0.2 wt% and drops down after increase in percentage i.e. 1.0 wt %. However the same behaviour is found while testing the gas sensing response for these thin films, it is found that the the gas sensing response is more for 0.2 % Cu modified samples as compared to 0.0 and 0.3-1.0 wt % modified films. Figure 3 shows the Variation of Sensitivity of ZnO: Cu/CuO modified with different concentration of Cu/CuO (i.e. 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 wt %) at 1000 ppm LPG gas concentration. It is observed that remarkable sensitivity of ZnO: Cu/CuO samples modified with 0.2 wt % Cu/CuO are very high (SF= $5x10^6$) at an operating temperature of 44$^o$C as compare to 0.0, 0.1, 0.3, 0.4 and 0.5 wt% samples.

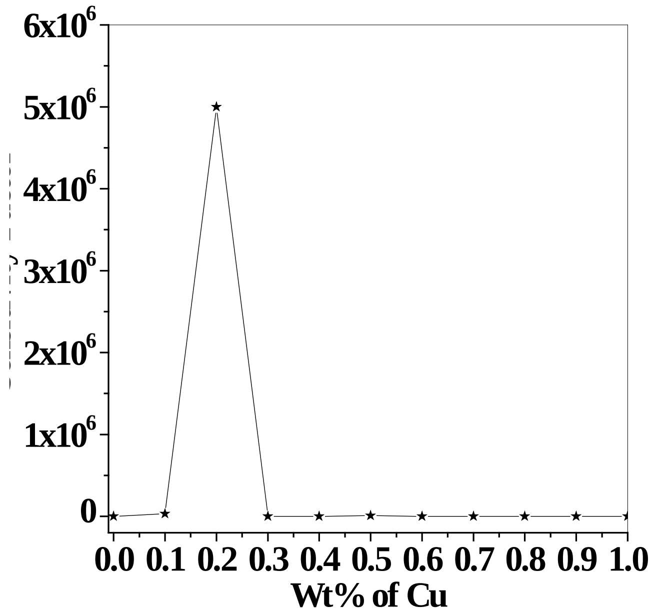



**Fig.3Variation of Sensitivity of ZnO:Cu/CuO modified with different concentration of Cu/CuO (i.e. 0.0,0.1,0.2, 0.3, 0.4, 0.5wt %) at 1000 ppm LPG gas concentration.**

Similarly, it can be seen that 0.4 Wt % also shows the noticeable sensitivity (SF = 230) as compare to 0, 0.2, 0.3 and 0.5 weight percentage modified samples. It is reported by P. S. More et al. [1, 2] the increase LPG sensitivity properties of samples prepared by spray pyrolysis may be due to the smaller surface area leading to the higher sensitivity of $SnO_2$: CuO commercially available powder.

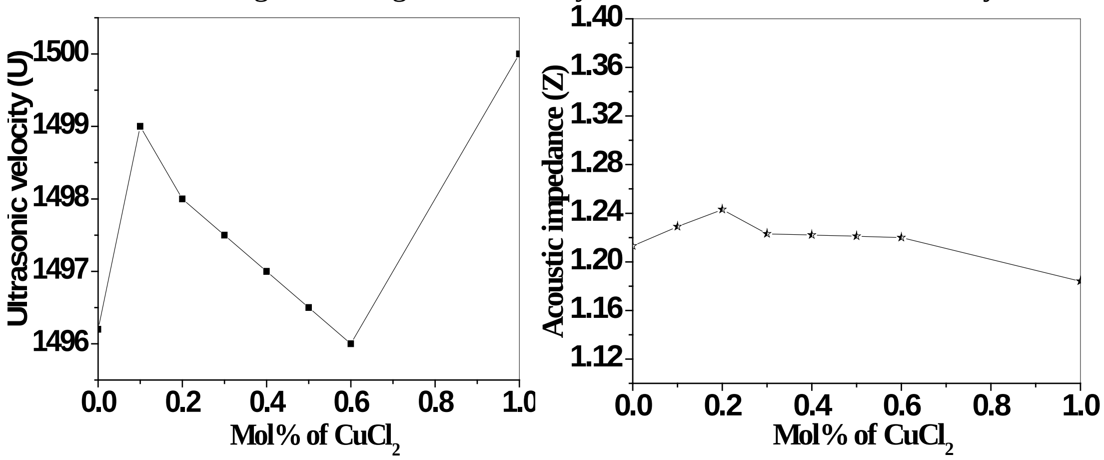



**Figure 4 (a)Variation of Ultrasonic velocity with mol% of Zn/$CuCl_2$,(b)Acoustic impedance with mol% of Zn/$CuCl_2$**

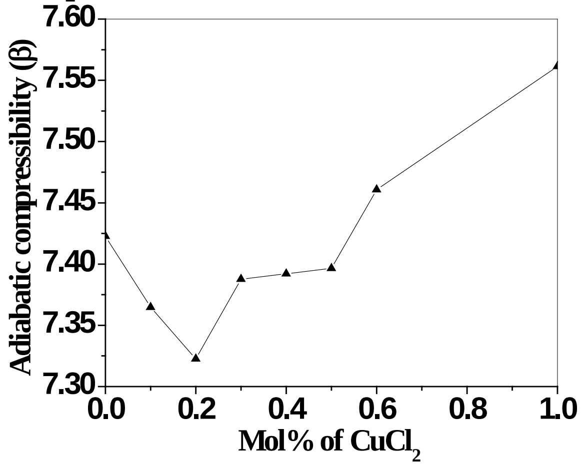



**Figure 4 (c)Variation of Adiabatic compressibility with mol% ofZn/$CuCl_2$**

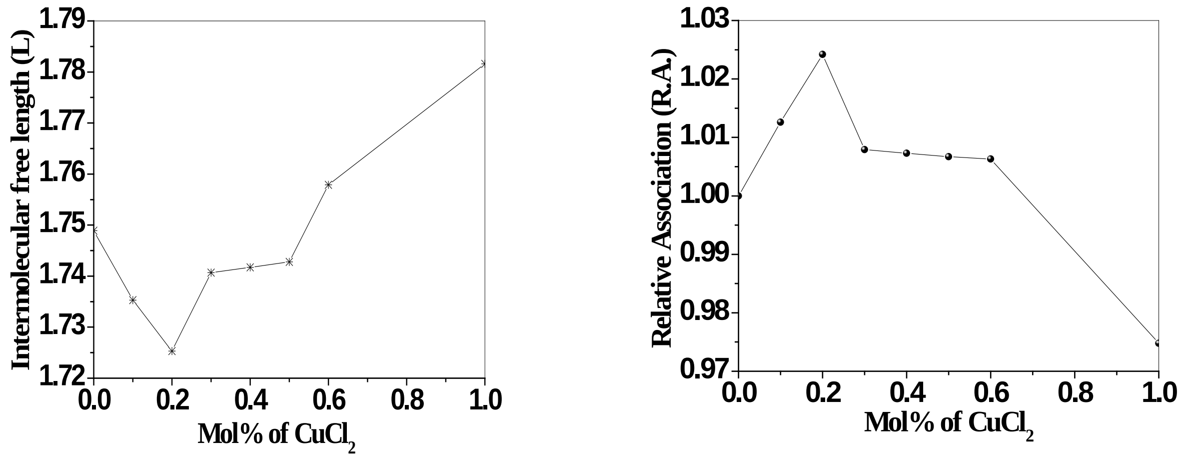



**Figure 4 (d)Variation of intermolecular free length (L), (e) Relative association (R.A.) with mol% of Zn/$CuCl_2$**

It can be observed from ultrasonic parameters (fig. 4) that are adiabatic compressibility, intermolecular length is low at only 0.2 weight percentage samples however, Ultrasonic velocity, acoustic impedance and relative association is high, while for higher concentration sample (0.3-1.0 wt% samples) the adiabatic compressibility, intermolecular free length is high. According to microstructure and grain size is concerned, 0.2 wt.% samples has very low practical size and uniform distribution of particle are see in the XRD pattern this may be the cause that enhancing the sensitivity.In case of adiabatic compressibility and inter molecular free length of 0.1 and 0.2 wt % is less as compared to 0.0 and 0.3-1.0 wt% samples

## 4. Conclusion:

The ZnO: Cu/CuO gas sensors were fabricated by spray pyrolysis There specific gas sensing characteristics were investigated and verified with ultrasonic parameter. LPG Gas sensing studies at 0.1 wt% Cu/CuO modified samples is indeed a good LPG sensor, possessing high sensitivity (SF=5x$10^6$) at very low temperature (i.e. 44$^o$C).

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