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International Journal For Research in Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 7 **Issue:** VIII **Month of publication:** August 2019

DOI: http://doi.org/10.22214/ijraset.2019.8065

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International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.177
Volume 7 Issue VIII, Aug 2019- Available at www.ijraset.com

Related Acoustical Parameters and Ultrasonic Velocity of substituted Pyrazole Carboxylic Acid derivatives at 305K in 80% (DMF+Water) Mixture at Different Concentrations

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Abstract: ***Ultrasonic study of substituted pyrazole carboxylic acid derivatives in 80% DMF-water at 305K is done. The experimental data is used to calculate Ultrasonic velocity, density, adiabatic compressibility (β_S), intermolecular free length (L_f) and specific acoustic impedance (Z). These acoustic parameters are used to explain the interaction taking place in the solutions.***
Keywords: substituted pyrazole carboxylic acid derivatives, acoustic parameters and interactions in solution

I. INTRODUCTION

Molecular structure and their interactions in solution is always received importance in various field of sciences. Ultra sound and ultrasonic interferometer significantly used in estimation of molecule interactions such as inter and intra ionic or molecular interactions. Since from last few decades ultra sound and ultrasonic interferometric investigation extensively used to understand molecular interactions in liquid. Study of Complex formation in ternary liquid mixtures of heterocyclic compounds, viz. pyridine and quinoline with phenol in benzene has been reported through ultrasonic velocity measurements (at 2 MHz) in the concentration range of 0.010–0.090 at varying temperatures of 35, 45 and 55 °C.[1] Viscometric and ultrasonic studies have been carried out in n-hexane solutions, containing equimolar 1 concentration from 0.02 to 0.2 M of aromatic ketones and N-methylaniline (NMANI), at 303.15 K and at atmospheric pressure.[2] The density, viscosity and ultrasonic velocity of aqueous Promethazine hydrochloride have been studied at 302.15 K. to determined free volume, internal pressure and Rao's constant and Wada's constant.[3] Determination of refractive index, density, molar refraction and polarizability constant of substituted N, N'-bis (salicyliden)-arylmethanediamines in different binary mixture refractometricallyis studied.[4] Density, viscosity and ultrasonic velocity studies of carbo group containing symmetric double Schiff bases solutions at 303is determined.[5] Molecular interactions in strong electrolytes-Metal chlorides in aqueous medium at temperatures and 2MHz frequency is reported by Ultrasonic studies.[6] Synthesis, ,charactrization, ultrasonic studies and application of a thiophene–pyrrole copolymer as an efficient adsorbent for removal of methylene blue is done. [7] Apparent molal volume, apparent molal compressibility, relative Association And Solvation Number of Substituted-N, N'bis (Salicyliden)-arylmethanediamines in 80% DMF+ water System at 300K is reported. [8] Viscosity coefficient (A, B) have been investigated from the the ultrasonic velocity and density measurements of substituted heterocyclic drugs to investigated solute-solvent interaction and solute-solute interaction.[9] acoustic, transport, refractive, and high-temperature volumetric data of substituted benzylamines is measured.[10] Synthesis, uitrasonic study and spectroscopic studies of new azo ligands Schiff base and amines derived of 5-phenylazo-2-hydroxybenzaldehyde have been reported.[11] Adiabatic compressibility, apparent molal volume, apparent molal compressibility and solvation number of aminopyrimidine in polar solvent is investigated.[12] Ultrasonic velocity and density measurements of some substituted pyrazolines in 70% acetone-water mixture at 303K is reported.[13] The apparent molar volume ($\emptyset_v$), apparent molar compressibility ($\emptyset_K$) and the viscosity B-coefficient ,density, ultrasonic velocity and viscosity of four pharmaceutically significant drugs were measured in methanol at 298K.[14] Estimation of adiabatic compressibility (β), apparent molal compressibility (k), apparent molal volume (v), intermolecular free length (Lf), relative association (RA) and specific acoustic impedance (Z) for solutions of 4-ethylthiocarbamidophenol (ETP) at different molar concentrations (i.e. 0.1M, 0.075M, 0.050M and 0.025M) and 300 K in 70% compositions of ethanol-water mixtures are done.[15]Studies on molecular interaction in ternary liquid mixtures by ultrasonic velocity measurementsis reported. [16] Acoustic properties like apparent molal volume, apparent molal compressibility, intermolecular free length, specific acoustic impedance and relative association have been determined for 2-hydroxy-5-chloro substituted chalconedibromides in ethanol have been carried out at 303K in the concentration range 0.05 to 0.005 mol dm-3 in

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100% ethanol.[17] Acoustical parameters such as adiabatic compressibility (κ), free length (L_f), internal pressure (π_i), molar volume (V_m) and available volume (V_a) have been used to study the molecular interactions and the complexes of heterocyclic aromatic compoundsare determined.[18] A survey of the literature indicates that no acoustical data on substituted pyrazole carboxylic acid derivatives has been produced. In the present work, different properties such as Ultrasonic velocity, density, adiabatic compressibility (β_S), intermolecular free length (L_f) and specific acoustic impedance (Z) in 80% (DMF+Water) mixture at different concentrations of ligand at 305K. have been evaluated

1) Ligand A (LA)= 1- phenyl-3-(4'- methyl) phenyl-1H- pyrazol-4-carboxylic acid
2) Ligand B (LB)=1- phenyl-3-(4'- bromo) phenyl-1H- pyrazol-4-carboxylic acid
3) Ligand C (LC)=1- phenyl-3-(4'- ethyl) phenyl-1H- pyrazol-4-carboxylic acid
4) Ligand D (LD)=1,3-diphenyl-1H- pyrazol-4-carboxylic acid

II. THEORY AND FORMULAE

Sound speeds can be measured using a single frequency ultrasonic interferometer. The ultrasonic waves of known frequency produced by a quartz crystal are reflected by a movable metallic plate kept parallel to the quartz plate. When the state of acoustic resonance is reached due to the formation of standing waves, an electrical reaction occurs on the generator driving the quartz plate and its anode current becomes maximum. The micrometer is slowly moved until the anode current meter on a high frequency generator shows a maximum. The distance thus moved by the micrometer gives the values of wavelength.

The distance traveled by micrometer screw to get one maximum in ammeter (D) is used to calculate wavelength of ultrasonic wave using following relation.

$$2D = \lambda \quad (1)$$

Where, λ is wavelength and D is distance in mm.

From the knowledge of the wavelength, the ultrasonic velocity can be obtained by the relation.

$$\text{Ultrasonic velocity (U)} = \lambda \times \text{Frequency} \times 10^3 \quad (2)$$

Using the measured data some acoustical parameters can be calculated using the standard relations.

The adiabatic compressibility of solvent and solution can be calculated by using equations.

$$\text{Adiabatic compressibility of solution } (\beta s) = 1/ U_s^2 \times d_s \quad (3)$$

$$\text{Adiabatic compressibility of solvent } (\beta_0) = 1/ U_0^2 \times d_0 \quad (4)$$

The acoustic impedance (Z) is calculated using equation.

$$\text{Acoustic impedance (Z)} = U_s \times d_s \quad (5)$$

Where, U_0 and Us are ultrasonic velocity in solvent and solution respectively.

d_0 and ds are density of solvent and solution respectively.

The apparent molal volume (ϕ_v) and apparent molal compressibility (ϕ_k) are given by following equations.

$$\text{Apparent molal volume } (\phi_v) = \frac{M}{d_s} + \frac{(d_o - d_s)\times 10^3}{(m d_s d_0)} \quad (6)$$

$$\text{Apparent molal compressibility } (\phi_k) = \frac{1000(\beta_s d_o - \beta_o d_s)}{m d_s d_o} + \frac{\beta_s M}{d_s} \quad (7)$$

Where, d_o and d_s are the densities of the pure solvent and solution, respectively.

m is the molality and M is the molecular weight of solute.

β_o and $\beta_s$are the adiabatic compressibility of pure solvent and solution respectively.

According to the studies intermolecular free length (L_f) is given by.

$$\text{Intermolecular free length } (L_f) = K\sqrt{\beta s} \quad (8)$$

The constant K is called the Jacobson's constant.

The value of Jacobson's constant can be calculated by using relation.

$$K = (93.875 + 0.375 \times T) \times 10^{-8} \quad (9)$$

Where, T is the temperature at which experiment is carried out.

The relative association (R_A) is given by the equation.

$$\text{Relative association } (R_A) = \left(\frac{d_s}{d_o}\right) \times \left(\frac{U_o}{U_s}\right)^{1/3} \quad (10)$$

The solvation number (Sn) is given by the equation.

$$\text{Solvation number (Sn)} = \phi_k / \beta_0 \times (M/ d_0) \quad (11)$$

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III. RESULTS AND DISCUSSION

Acoustic parameters are helpful to understand behavior of solute and solvent molecules in solutions. Changes in the values of these parameters with concentration are very important to explain number of factors.

From the table I, ultrasonic velocity is directly proportional to the concentration. Figure I shows the variation of ultrasonic velocity with concentration. In more concentrated solution the possibility of making hydrogen bond increases which gives packed structure and accordingly ultrasonic velocity increases. Ultrasonic velocity increases on increasing the concentration of solute may be attributed to cohesion brought about by the association among the molecule and greater solute-solvent interaction.

Table I shows that the adiabatic compressibility (β_s) increases with decrease in the value of concentrations. This is as per general trend observed for the electrolytic solutions. In more concentrated solution, more cohesion is expected and this lead to a decrease in β_s. The decrease in β_s results in an increase in the value of ultrasonic velocity. Decrease of concentration of solution with increase of adiabatic compressibility may be due to the dispersion of solvent molecules around ions supporting weak ion solvent interactions.

Table I suggests that intermolecular free length is more in more dilute solutions. Figure III shows the variation of intermolecular free length with concentrations. Extensive use of intermolecular free length (L_f) is made to study the intermolecular interactions in mixtures. In many cases, the value of intermolecular free length (L_f) corresponds to the molecular shape, that is the L_f in the molecules having the spherical and/or symmetrical shape is short and the short L_f leads to a high speed of sound. Decrease in intermolecular free length leads to positive deviation in sound velocity and negative deviation in compressibility.

Specific acoustic impedance (Z) is the impedance offered to sound wave by the components of mixture. Table I suggests that as the concentration decreases the specific acoustic impedance decreases. Figure IV shows the variation of specific acoustic impedance with concentrations. Mathematically it is directly proportional to ultrasonic velocity. Increase in specific acoustic impedance with increase in concentration suggests associative molecular interactions

IV. CONCLUSIONS

The adiabatic compressibility value decreases with increasing concentration indicates formation of strong hydrogen bonding between solute and solvent. The value of intermolecular free length corresponds to the molecular shape. The increase in apparent molal volume with decrease in concentration indicates the existence of strong ion-solvent interaction. The increase in value of apparent molal compressibility with decrease in concentrations shows the weak electrostatic attractive force in the vicinity of ions causing electrostatic salvation of ions.

Table- I

Ultrasonic velocity, Density, Adiabatic compressibility (β_S), Intermolecular free length (L_f) and Specific acoustic impedance (Z) in 80% DMF solvent at 305K

Conc. (m) (mol lit^{-1})	Density (ds) (kg m^{-3})	Ultrasonic Velocity (Us) (m s^{-1})	Adiabatic Compressibility (β_S) x10^{-9} (m^2N^{-1})	Intermolecular free length (L_f) x10^{-11} (m)	Specific acoustic impedance (Z) x10^5 (kg $m^{-2}s^{-1}$)
Ligand LA in 80% (DMF +Water) solvent					
0.01	1126.3	880.2	1.1465	6.9879	9.911
0.005	1124.1	837.2	1.2692	7.3523	9.410
0.0025	1122.5	808.4	1.3632	7.6197	9.074
0.00125	1121.4	800.0	1.3933	7.7034	8.971
0.000625	1119.9	790.8	1.4270	7.7983	8.856
Ligand LB in 80% (DMF +Water) solvent					
0.01	1225.9	885.2	1.0410	6.6581	10.851
0.005	1223.9	852.0	1.1255	6.9230	10.427
0.0025	1222.3	847.6	1.1387	6.9644	10.365
0.00125	1220.9	833.6	1.1787	7.0857	10.177
0.000625	1219.8	826.4	1.2004	7.1502	10.080
Ligand LC in 80% (DMF +Water) solvent					

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0.01	1225.1	859.6	1.1046	6.8591	10.534
0.005	1222.7	846.0	1.1427	6.9762	10.347
0.0025	1221.9	830.8	1.1856	7.1065	10.151
0.00125	1220.8	815.2	1.2326	7.2456	9.951
0.000625	1219.6	813.2	1.2399	7.2667	9.917
Ligand LD in 80% (DMF +Water) solvent					
0.01	1253.6	850.4	1.103	6.8540	10.660
0.005	1251.2	835.2	1.145	6.9854	10.450
0.0025	1249.6	825.2	1.175	7.0745	10.311
0.00125	1248.3	820.0	1.191	7.1237	10.237
0.000625	1247.2	808.8	1.225	7.2255	10.087

Fig -1: Plot of Ultrasonic Velocity(Us) m s^{-1} Vs concentration (mol/lit) in 80% DMF solvent

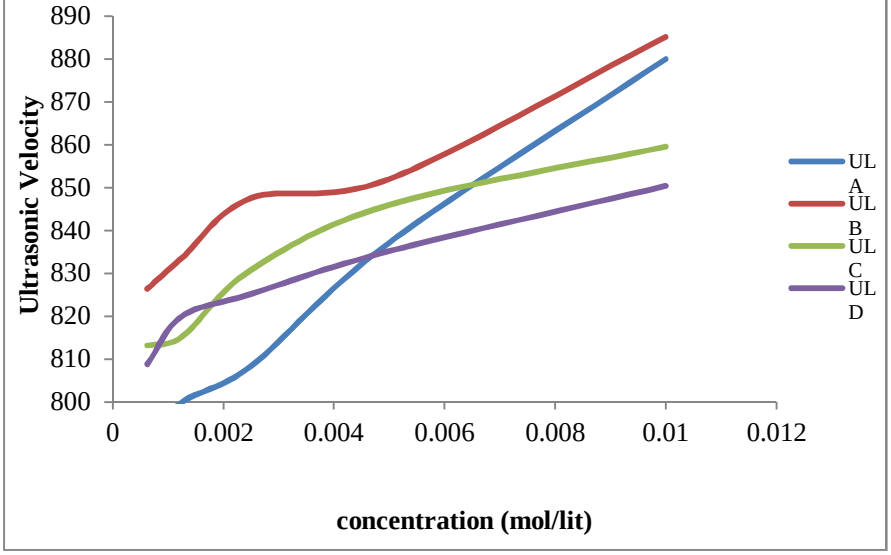
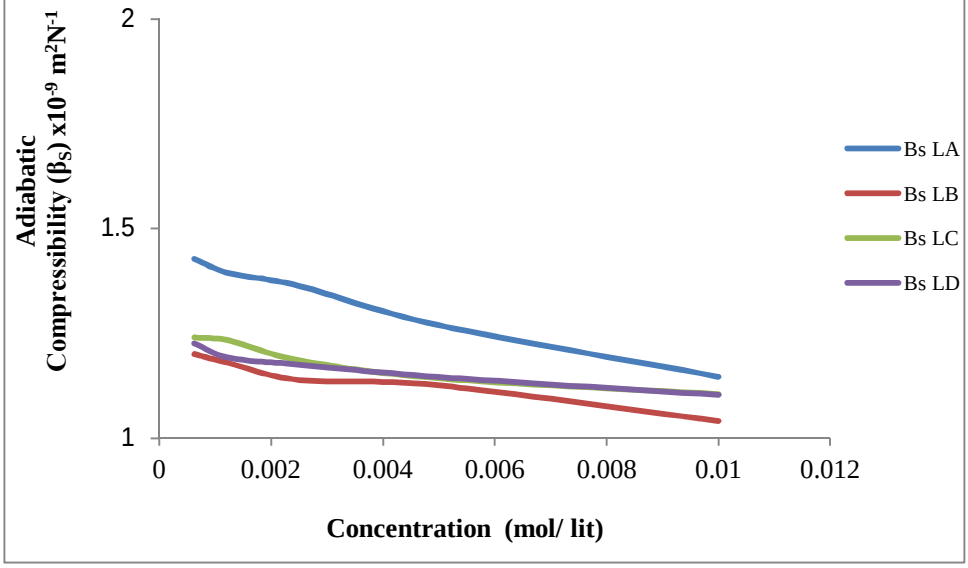
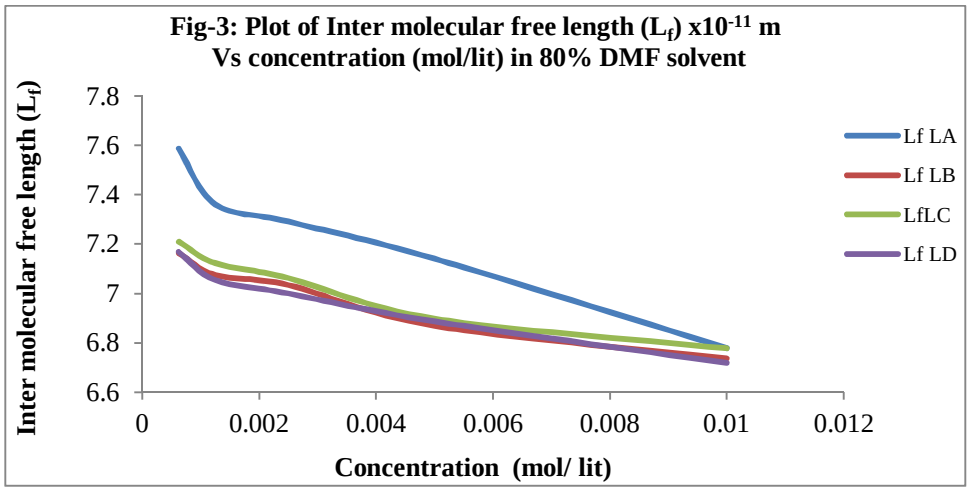
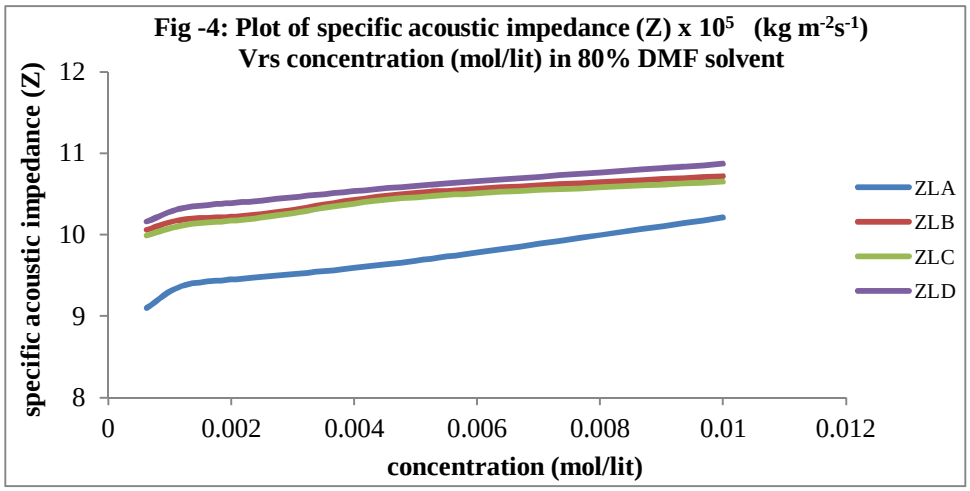


Fig-2: Plot of Adiabatic Compressibility (β_S) x10^{-9} m^2N^{-1} Vs concentration (mol/lit) in 80% DMF solvent



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V ACKNOWLEDGEMENT

The authors gratefully acknowledge Head, Department of Chemistry, Govt. Vidarbha Institute of Science and Humanities, Amravati for providing necessary facilities and help when needed for the work.

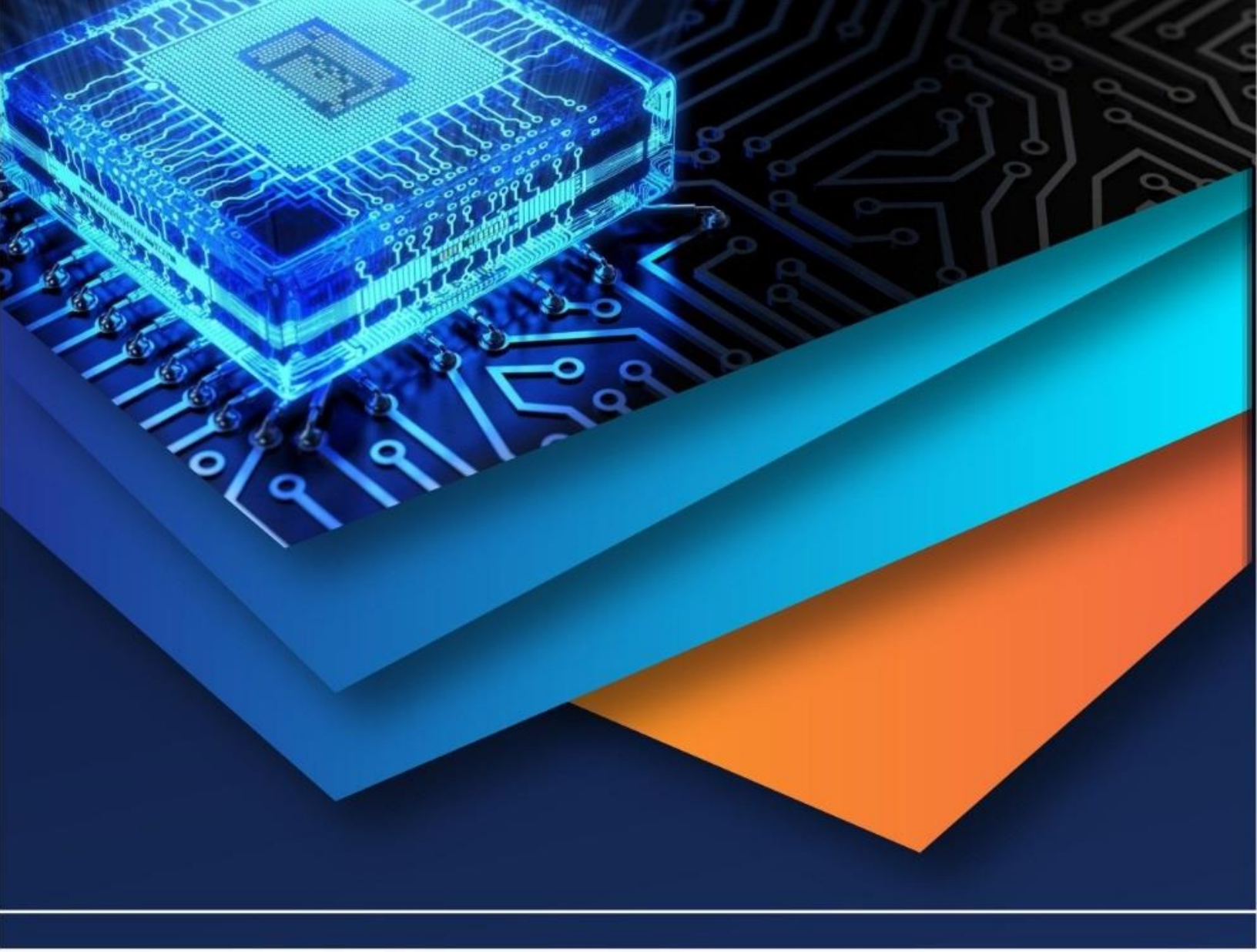
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