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Ultrasonic Velocity and Related Acoustical Parameters of N–(2-Hydroxybenzylidene)-3-Substituted Pyridine-2-Amine Schiff Bases in Ethanol-Water Mixture

Mrunal M. Mahajan* and Pravin B. Raghuwanshi

*Brijlal Biyani Science College, Amravati – 444602 (M.S.), **INDIA**

Email: mrunalmahajan72@gmail.com

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ABSTRACT

In order to study the molecular interactions of N–(2-hydroxybenzylidene)-3-substituted pyridine-2-amine Schiff bases in ethanol-water mixture, interferometric measurements were done and various acoustical parameters like ultrasonic velocity (V), adiabatic compressibility (β_s), apparent molar volume (ϕ_V) and intermolecular free length (L_f) were determined. The densities and velocities of the ligand solutions were used to evaluate these parameters for ethanol-water system of different concentration at 293, 297 and 300 K, which helps in understanding structural interaction of water molecules and organic solvent molecules with substituted Schiff bases.

Keywords: Substituted Schiff bases, molecular interaction, acoustical, densities, velocities.

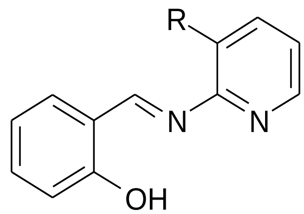
INTRODUCTION

Ultrasonic is the branch of acoustic, which consists of waves of high frequencies. It deals with the properties and behaviour of elastic waves of frequencies more than 20 KHz. The use of ultrasound is one of the well-recognized approaches in the industrial procedures, in medicinal science [1-3], in locating objects and measuring distances, in communication [4] and for the study of molecular interactions in fluids [5-10]. The study of molecular interaction in liquids provides valuable information regarding internal structure, molecular association, complex formation, etc. Velocity measurement combining with other physical quantities provides information about number of parameters related to ultrasonic velocity like compressibility, excess enthalpy, hydrogen bonding, intermolecular free length, molecular interaction, relative association, acoustic impedance, latent heat of vaporization, specific heat ratio, miscibility and compatibility of blends and many more [11].

The active nature of Schiff base derivatives in biological, chemical and medicinal sciences have prompted the researchers towards the study of molecular interactions of organic solvent molecules with substituted Schiff bases which provides the nature and strength of interactions. Thus, the number of workers have investigated ultrasonic studies of Schiff base solutions and reported about the variation in ultrasonic velocity with ion concentration and also studied solute-solvent interaction, solvation number and other ultrasonic parameters [12-16]. Hence in the present study, attempt has been made to study the molecular interactions of the following substituted Schiff base ligands in the suitable percentage of ethanol – water mixture at different temperatures by acoustical investigations.

1. N-(2'-hydroxybenzylidene) pyridine-2-amine (A_1)
2. N-(2'-hydroxybenzylidene)-3-hydroxy pyridine-2-amine (A_2)
3. N-(2'-hydroxybenzylidene)-3-nitropyridine-2-amine (A_3)
4. N-(2'-hydroxybenzylidene)-3-methylpyridine-2-amine (A_4)

The structure of the ligand is shown in fig 1.



Where,
R = -H, -OH, $-NO_2$, $-CH_3$

N - (2 - hydroxybenzylidene)
pyridine - 2 - amine

Fig 1

MATERIALS AND METHODS

Experimental: All the chemicals used for synthesis were of L.R. grade. The ligands (A_1-A_4) were recrystallized before use. Ethanol was purified using standard procedure. All the working solutions were freshly prepared from the deionized water. The 0.01M solution of each ligand was prepared in different percentage (75%, 80%, 85%, 90%, 95% and 100%) of ethanol-water mixture. The density and the ultrasonic velocity measurements of the ligand solutions were done at 293, 297 and 300 K following the standard protocol.

Instrumentation: All the weighing was made on Citizen CY 104 one pan digital balance. The densities of the solution were determined by standardize capillary pyknometer having a bulb of volume of about 10 cm^3 and capillary having an internal diameter of 1 mm. In the present investigation, a variable path ultrasonic interferometer from Mittal enterprises, New Delhi, Model MX-3 was used to measure the ultrasonic velocity in liquid mixtures and solutions. The working frequency of interferometer was 1 MHz with the accuracy of ±0.03%.

RESULTS AND DISCUSSION

The present work deals with interferometric measurements like ultrasonic velocity (V), adiabatic compressibility (β_s), apparent molar volume (ϕ_v) and intermolecular free length (L_f), which reveals the structural interaction of substituted Schiff bases. These acoustic parameters for ligands A_1, A_2, A_3 and A_4 in varying percentage of ethanol-water, studied at three different temperatures are calculated from the ultrasonic velocity obtained. The results are given in tables 1 to12.

Table 1: Acoustic Parameters at different percentages of ethanol-water mixture.
System: Ligand – A_1, Temp = 293 K

% Ethanol	d_s x 10^3 (kg m^{-3})	V x 10^3 (m sec^{-1})	β_s x 10^{-10} (pa^{-1})	ϕ_v x 10^{-3} (m^3 mol^{-1})	L_f x 10^{-1} (m^{-1})
75	0.87594	1.964	0.2960	-1719.84	336.21
80	0.86999	1.9758	0.2944	-2300.10	335.34
85	0.83164	1.9706	0.3096	1267.33	343.89
90	0.81379	1.9676	0.3174	2444.01	348.17
95	0.8057	1.9682	0.3204	973.18	349.81
100	0.79878	1.793	0.3894	608.87	385.65

Table 2: Acoustic Parameters at different percentages of ethanol-water mixture.
System: Ligand – A_2, Temp = 293 K

% Ethanol	d_s x 10^3 (kg m^{-3})	V x 10^3 (m sec^{-1})	β_s x 10^{-10} (pa^{-1})	ϕ_v x 10^{-3} (m^3 mol^{-1})	L_f x 10^{-1} (m^{-1})
75	0.8752	1.8564	0.3316	-1604.84	355.85
80	0.86408	1.987	0.2931	-1493.86	334.59
85	0.83553	1.964	0.3103	725.55	344.24
90	0.81868	1.8354	0.3626	1728.12	372.14
95	0.81696	1.7402	0.4042	-721.28	392.91
100	0.80299	1.5446	0.5220	-28.86	446.50

Table 3: Acoustic Parameters at different percentages of ethanol-water mixture.
System: Ligand – A_3, Temp= 293 K

% Ethanol	d_s x 10^3 (kg m^{-3})	V x 10^3 (m sec^{-1})	β_s x 10^{-10} (pa^{-1})	ϕ_v x 10^{-3} (m^3 mol^{-1})	L_f x 10^{-1} (m^{-1})
75	0.87027	1.8082	0.3514	-922.86	366.37
80	0.85605	1.7718	0.3721	-372.07	376.99
85	0.83567	1.8128	0.3641	740.16	372.92
90	0.81657	1.777	0.3878	2079.94	384.86
95	0.81237	1.6096	0.4751	7.50	425.98
100	0.8043	1.6064	0.4818	-196.08	428.97

Table 4: Acoustic Parameters at different percentages of ethanol-water mixture.
System: Ligand – A_4, Temp= 293 K

% Ethanol	d_s x 10^3 (kg m^{-3})	V x 10^3 (m sec^{-1})	β_s x 10^{-10} (pa^{-1})	ϕ_v x 10^{-3} (m^3 mol^{-1})	L_f x 10^{-1} (m^{-1})
75	0.87069	2.1086	0.2583	-1014.03	314.10
80	0.8606	2.1688	0.2470	-1027.20	307.16
85	0.83678	2.0002	0.2987	543.99	337.76
90	0.81761	2.1776	0.2579	1885.87	313.86
95	0.80842	2.239	0.2467	572.08	306.98
100	0.80132	1.9766	0.3194	228.73	349.27

Table 5: Acoustic Parameters at different percentages of ethanol-water mixture
System: Ligand – A_1, Temp= 297 K

% Ethanol	$d_s \times 10^3$ (kg m^{-3})	V x 10^3 (m sec^{-1})	$\beta_s \times 10^{-10}$ (pa^{-1})	$\phi_v \times 10^{-3}$ (m^3 mol^{-1})	$L_f \times 10^{-1}$ (m^{-1})
75	0.8588	1.7266	0.3906	568.58	389.99
80	0.8491	1.5942	0.4634	527.85	424.77
85	0.8327	1.5950	0.4720	1112.52	428.72
90	0.8201	1.5776	0.4900	1501.13	436.78
95	0.8169	1.6268	0.4626	-724.35	424.40
100	0.8042	1.6248	0.4710	-239.63	428.25

Table 6: Acoustic Parameters at different percentages of ethanol-water mixture
System: Ligand – A_2, Temp= 297 K

% Ethanol	$d_s \times 10^3$ (kg m^{-3})	V x 10^3 (m sec^{-1})	$\beta_s \times 10^{-10}$ (pa^{-1})	$\phi_v \times 10^{-3}$ (m^3 mol^{-1})	$L_f \times 10^{-1}$ (m^{-1})
75	0.8577	1.6320	0.4378	732.79	412.86
80	0.8554	1.6216	0.4446	-312.89	416.07
85	0.8204	1.3998	0.6221	2940.50	492.17
90	0.8195	1.3788	0.6419	1613.10	499.94
95	0.8104	1.3848	0.6435	279.31	500.57
100	0.8061	1.4454	0.5938	-516.52	480.83

Table 7: Acoustic Parameters at different percentages of ethanol-water mixture.
System: Ligand – A_3, Temp = 297 K

% Ethanol	$d_s \times 10^3$ (kg m^{-3})	V x 10^3 (m sec^{-1})	$\beta_s \times 10^{-10}$ (pa^{-1})	$\phi_v \times 10^{-3}$ (m^3 mol^{-1})	$L_f \times 10^{-1}$ (m^{-1})
75	0.8520	1.7596	0.3791	1543.00	384.19
80	0.8399	1.7482	0.3896	1875.31	389.47
85	0.8346	1.6880	0.4205	888.19	404.63
90	0.8210	1.6332	0.4566	1416.05	421.67
95	0.8191	1.3310	0.6892	-1001.88	518.02
100	0.8036	1.4036	0.6316	-93.72	495.92

Table 8: Acoustic Parameters at different percentages of ethanol-water mixture
System: Ligand – A_4 Temp= 297 K

% Ethanol	$d_s \times 10^3$ (kg m^{-3})	V x 10^3 (m sec^{-1})	$\beta_s \times 10^{-10}$ (pa^{-1})	$\phi_v \times 10^{-3}$ (m^3 mol^{-1})	$L_f \times 10^{-1}$ (m^{-1})
75	0.8527	1.6430	0.4344	1416.96	411.30
80	0.8457	1.6156	0.4530	1021.58	419.99
85	0.8267	1.6292	0.4557	2008.62	421.25
90	0.8258	1.6586	0.4402	665.88	414.00
95	0.8121	1.6204	0.4690	11.87	427.33
100	0.8029	1.5826	0.4973	-9.59	440.04

Table 9: Acoustic Parameters at different percentages of ethanol-water mixture
System: Ligand – A_1, Temp= 300 K

% Ethanol	$d_s \times 10^3$ (kg m^{-3})	V x 10^3 (m sec^{-1})	$\beta_s \times 10^{-10}$ (pa^{-1})	$\phi_v \times 10^{-3}$ (m^3 mol^{-1})	$L_f \times 10^{-1}$ (m^{-1})
75	0.8586	2.1832	0.2444	595.76	310.44
80	0.8584	1.9574	0.3041	-739.64	346.29
85	0.8539	2.0056	0.2911	-1873.48	338.85
90	0.8448	2.0510	0.2814	-2079.75	333.13
95	0.8312	1.8466	0.3528	-2846.39	373.01
100	0.8178	1.8348	0.3632	-2307.02	378.49

Table 10: Acoustic Parameters at different percentages of ethanol-water mixture
System: Ligand – A_2, Temp= 300 K

% Ethanol	$d_s \times 10^3$ (kg m^{-3})	V x 10^3 (m sec^{-1})	$\beta_s \times 10^{-10}$ (pa^{-1})	$\phi_v \times 10^{-3}$ (m^3 mol^{-1})	$L_f \times 10^{-1}$ (m^{-1})
75	0.8565	1.6432	0.4324	895.13	412.96
80	0.8445	1.8122	0.3606	1200.75	377.11
85	0.8372	1.8152	0.3625	480.58	378.10
90	0.8215	1.7890	0.3804	1312.38	387.31
95	0.8181	1.7328	0.4071	-896.71	400.68
100	0.8144	1.9858	0.3114	-1780.39	350.43

Table 11: Acoustic Parameters at different percentages of ethanol-water mixture
System: Ligand – A_3, Temp= 300 K

% Ethanol	$d_s \times 10^3$ (kg m^{-3})	V x 10^3 (m sec^{-1})	$\beta_s \times 10^{-10}$ (pa^{-1})	$\phi_v \times 10^{-3}$ (m^3 mol^{-1})	$L_f \times 10^{-1}$ (m^{-1})
75	0.8554	1.6980	0.4054	1074.01	399.88
80	0.8480	2.2114	0.2411	740.94	308.39
85	0.8450	1.8278	0.3542	-581.51	373.77
90	0.8303	1.6116	0.4637	55.75	427.66
95	0.8248	1.8062	0.3716	-1852.11	382.84
100	0.8155	1.3630	0.6601	-1903.26	510.22

Table 12: Acoustic Parameters at different percentages of ethanol-water mixture
System: Ligand – A_4, Temp = 300 K

% Ethanol	$d_s \times 10^3$ (kg m^{-3})	V x 10^3 (m sec^{-1})	$\beta_s \times 10^{-10}$ (pa^{-1})	$\phi_v \times 10^{-3}$ (m^3 mol^{-1})	$L_f \times 10^{-1}$ (m^{-1})
75	0.8525	1.9300	0.3149	1445.91	352.42
80	0.8362	1.8888	0.3352	2367.73	363.59
85	0.8238	2.0260	0.2957	2430.94	341.51
90	0.8195	1.9720	0.3138	1609.16	351.79
95	0.8124	1.8098	0.3758	-38.25	384.98
100	0.8058	1.6374	0.4629	-460.38	427.27

Adiabatic compressibility (β_s): Adiabatic compressibility (β_s) depends on the structure of the liquid such as shape, size, branching and presence of aromatic ring which is important in considering geometrical fit of the solute into the ordered form of the aqueous solvent surrounding these solutes [17]. From tables1-12 and fig. 2-4, it is observed that the β_s values of ligands mostly increase with increase in percentage of organic solvent at 293 K, 297 K and 300 K. This may be due to the decrease in the number of free ions, as there is aggregation of solvent molecules around the ions. The positive β_s value indicates the existence of dispersive forces between molecules of mixtures. It also indicates loosely packed molecules in the mixture.

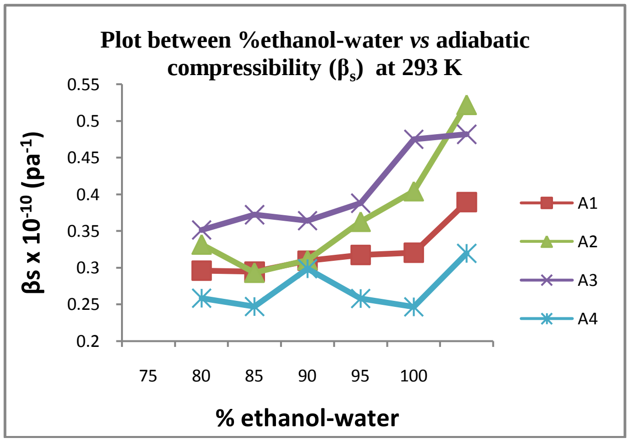


Fig. 2

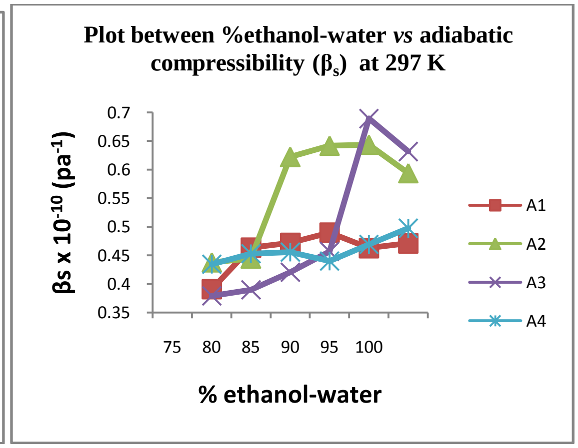


Fig. 3

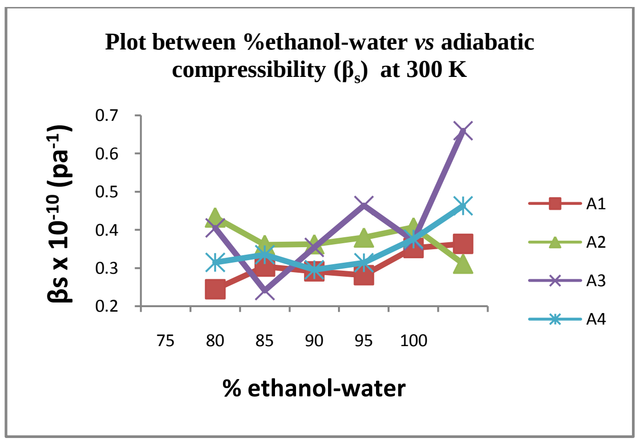


Fig.4

Apparent molar volume (ϕ_v): Apparent molar volume (ϕ_v) expresses the solute-solvent interactions in the solution. Tables 1–12 and fig. 5-7 shows that, ϕ_v value decreases with increase in the percentage of ethanol at 293 K, 297 K and 300 K. The change in ϕ_v with variation in concentration depends on the concentration of the salt, the nature and size of electrolyte ions and the dielectric constant [18]. It is also observed that ϕ_v values are negative for most of the compositions in ethanol indicating the compactness of medium. The negative values of ϕ_v indicate ionic and hydrophilic interactions in these systems, a strong ion-solute interaction and less complex ion formation and also the existence of smaller solute-solute interactions [19].

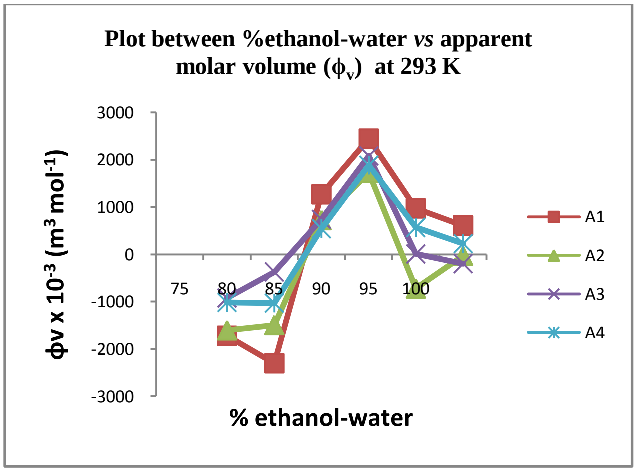


Fig. 5

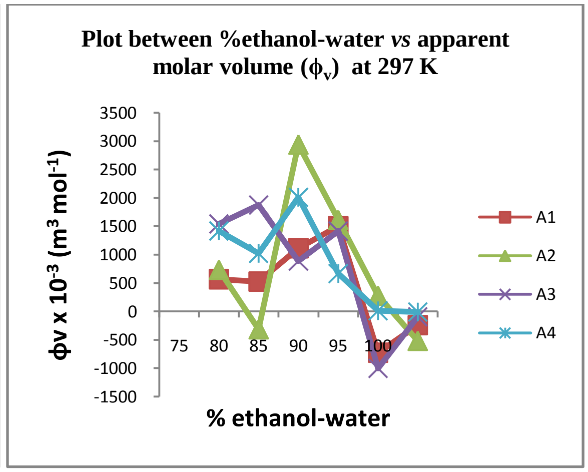


Fig. 6

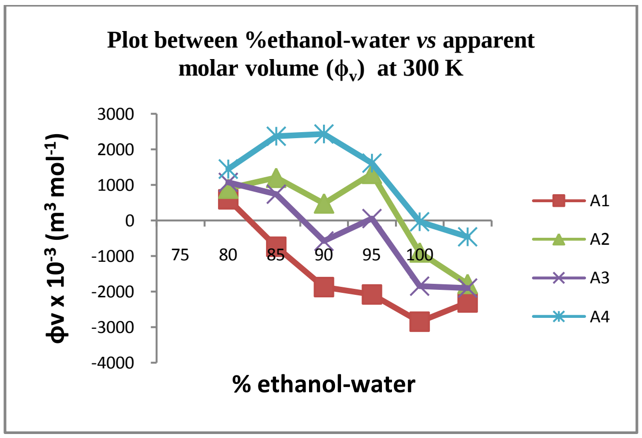


Fig. 7

Intermolecular free length (L_f): The intermolecular free length of a system is a measure of intermolecular attraction between the components in binary mixtures. Present study shows positive L_f values shows presence of dispersive forces between molecules of mixture. With increase in temperature, the ordered structure becomes less prominent and hence L_f increases. Table 1-12 and fig. 8-10 shows that interaction become weaker with increase in temperature as L_f increases. However, the trend is not prominent. L_f increases linearly with increase in concentration of ethanol suggesting structure promoting behaviour of the added solute, as there is significant ion-solvent interaction [20].

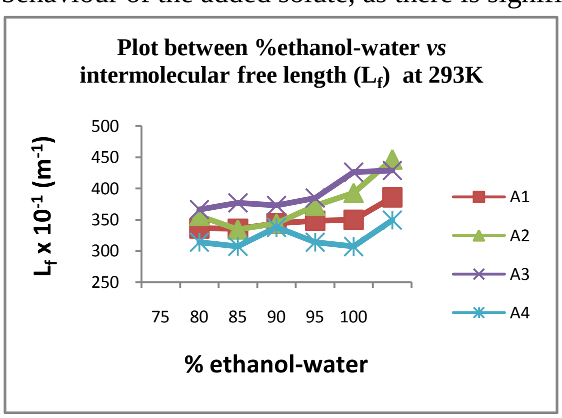


Fig 8

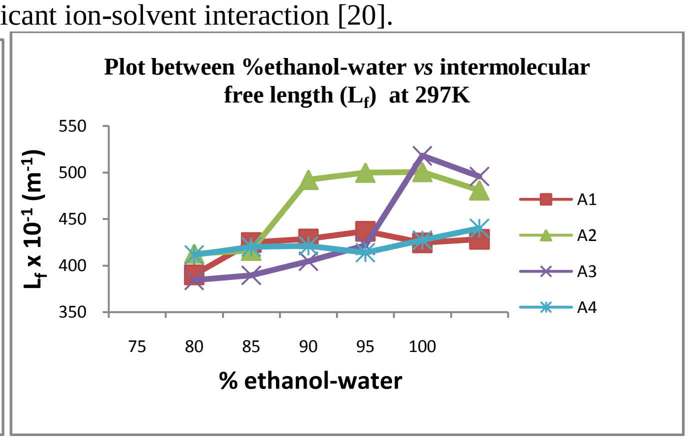


Fig 9

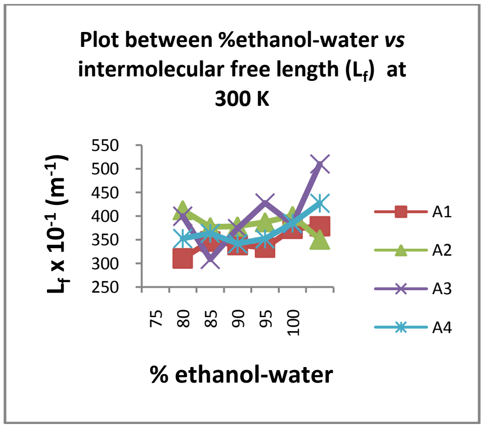


Fig. 10

APPLICATIONS

An acoustical investigation helps in understanding the intermolecular interactions like interactions between solute-solvent, solute-solute and ion-solvent. With this knowledge, one can easily find out the stability of the Schiff base ligands in the solution. This will further help in deciding the use of the respective Schiff base derivatives in biological, chemical and medicinal sciences.

CONCLUSIONS

From the present study it can be concluded that β_s and L_f values mostly increases with increase in percentage of organic solvent while the values of ϕ_v decreases at 293, 297 and 300 K. It is also observed that ϕ_v values are negative for most of the compositions in ethanol indicating the compactness of medium, strong ion-solute interaction and smaller solute-solute interactions. Thus study of acoustic properties helps in explaining how solute-solvent, solute-solute and ion-solvent interactions occur and are responsible for breaking and making of the structure in the solution.

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AUTHORS' ADDRESSES

1. **Mrunal Mahajan**
   Brijlal Biyani Science College, Amravati
   Email: mrunalmahajan72@gmail.com, Contact- 9096310826
2. **Dr. P. B. Raghuwanshi**
   Professor & Head, Dept. Of chemistry,
   Brijlal Biyani Science College, Amravati
   Email:pbraghuwanshi@gmail.com, Contact- +91 94221 55603