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CYCLIC VOLTAMMETRIC AND ACOUSTICAL STUDIES OF SOME Cu(II), Ni(II) AND Pb(II) COMPLEXES OF RED HE7B AT 303 K

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ABSTRACT

The cyclic voltammetric measurement and molecular interaction studies of Cu II), Ni(II) and Pb(II) complexes of red HE7B using DMSO were carried out at 303 *K*. The cyclic voltammetric were carried out at a stationary platinum electrode in DMSO with 0.1M tetra butyl ammonium per chlorate (TBAP) as a supporting electrolyte. The measured values of ultrasonic velocity, density, acoustical parameters, adiabatic compressibility and free length are evaluated. From the properties of these parameters the nature and strength of the interactions in these complexes and oxidation, reduction behaviours were discussed.

Keywords: **cyclic voltammetric, acoustical parameters, adiabatic compressibility and copper –azo coordination**

INTRODUCTION:

In recent years, ultrasonic technique has become a powerful tool for studying the molecular behaviour of liquid mixtures[1-3]. This is because of its ability of characterizing physic-chemical behaviour of liquid medium [4]-[5].The measurements of ultrasonic velocity have been adequately employed in understanding the molecular interactions in liquid mixtures. Molecular interaction studies can be carried out by spectroscopic [6-8] and non-spectroscopic [9-10] techniques. However, ultrasonic velocity [11-12] measurements have been widely used in the field of interactions and spectral aspect evaluation studies.

EXPERIMENTAL:

All the chemicals and reagents were used without further purification. The synthesis of all the coordination complexes was reported earlier [15, 16]. The electrochemical behaviours of Cu (II), Ni (II) and Pb (II) complexes of red HE7B were investigated. The electrochemical studies concerning these complexes have never been reported to our knowledge up to the present time. Experimental the electrochemical measurements were performed with a Princeton Applied Research model 173 potentiostat, a universal programmer model 175 and an X-Y recorder, model RE 0074. The one compartment electrochemical cell was equipped with a glassy carbon disc working electrode, a platinum plate as counter electrode and a reference electrode of calomel wire. All measurements were carried out in dimethylsulfoxide (DMSO) with 0.1 M tetra butyl ammonium per chlorate (TBAP) as supporting electrolyte. The solutions were carefully degassed and argon bubbling was stopped during measurements to ensure semi-infinite linear diffusion conditions. The ultrasonic velocity was measured at 303 K using a crystal interferometer with a high degree of accuracy operating at a frequency of 2 MHz the density was measured at 303 K using specific gravity bottle by the standard procedure.

RESULTS AND DISCUSSION:

The electrochemical behaviour of Cu (II), Pb (II) and Ni (II) complexes of red HE7B studied using cyclic voltammetry at a scan rate of the 0.1V/S after de aerating 10^{-3}M solution of the complexes in DMSO with tetra butyl ammonium per chlorate (TBAP) as a supporting electrolyte. The cyclic voltammogram of the red HE7B - copper complex shows that the oxidation and reduction of Cu (II) in the complex are characterized by a well defined redox peaks at 0.75 V (anodic) and 0.52 V (cathodic) vs. SCE that remained stable after the cycle. This process is usually assumed to be a single-electron reduction/oxidation of the couple Cu^{3+}/ Cu^{2+} // Cu^{2+}/Cu^{3+} in the metallic centre of the complex. In addition to the red HE7B - Pb (II) peak, the obtained oxidation peak at the negative potential side indicated that the processes take place on the metal centre of the complex. This peak describes a one-electron oxidation of Pb^{2+}/Pb^{3+}. The absence of the cathodic signal is indicative of a fast chemical reaction following the charge transfer step and instability of the electron. The cyclic voltammogram of the red HE7B - nickel complex shows that the oxidation and reduction of Ni (II) in the complex are characterized by a well defined redox peaks at 0.45 V (anodic) and 0.42 V (cathodic) vs. SCE that remained stable after the cycle. This process is usually assumed to be a single-electron reduction/oxidation of the couple Ni^{3+}/ Ni^{2+} // Ni^{2+}/Ni^{3+} in the metallic centre of the complex. The cyclic voltammogram of the complexes are shown in fig.2.

The Acoustical parameters of dye and its metal (II) complexes are shown in table.1 to table4. The average values of ultrasonic velocity may be increases and average values of adiabatic compressibility factor may be decreases in all the pH solution, none linearly with increasing concentration of dye. This can be explained by resorting to flickering cluster model of water. When the dye is dissolved in water, the dye molecules would first disrupt the open structure organization leaving the molecules in closely fitted helical cavities. The dye molecules can occupy both the nodes and voids of the water framework. Such an increase in close packed structures of water result in increased cohesion of water molecules leading to decrease in compressibility. This also results in may be increase of ultrasonic velocity. However, the adiiabatic compressibility (β), intermolecular free length (L_f) and acoustic impedance (Z) may be decrease with increase of concentration at 30^0C.

At low concentration dye-water, interaction dominates where as at high concentration dye-dye interaction dominates. Though the dye-solvent interaction may result from hydrogen bonding, dispersion and polar effects at lower concentration, the interactions like hydrogen bonding, which dominates, as dye is polar in nature. This indicates an increase in the effective six of the molecule in the path of ultrasonic wave. This is due to the complex formation between several dye macro molecule and water molecules.

In all the metal-dye complexes, the adiabatic compressibility factor (β) is may be less than the corresponding dyes of similar concentration. These suggest that salvation of dye complex may be increases which is indicated by the may be decrease of adiabatic compressibility factor. The increase in velocity near 4pH and 10pH may be due to the fact that there may be strong interaction between the solvent and the solute. A similar effect has been observed by Ramrece Sanyal (2001) [13]. From fig.3, to fig.8 the adiabatic compressibility and intermolecular free length decrease non-linearly with increase of concentration of metal complexes in all the solvents. The decrease is more pronounced at acidic pH for all metal complexes and at basic pH for pneumonia dyes by Rajagopalan and Sharma (2000) [14]. The decrease in compressibility at 4pH (copper complex) and 10pH (nickel complex) may be explained on the basic of close packing of the HE7B molecule in all the solvent, finally resulting in an increase in ionic repulsion. So, internal pressure decreases with an increase in the concentration of metal complexes.

Conc. %	**Solvents**	**U m / s**	**ρ Kg /m^3**	**$\eta\times10^3$ Nsm^{-2}**	**$\beta\times10^{10}$ $N^{-1}m^2$**	**Lf Å**	**$\pi i\times10^{-6}$ Pascal**
	DMSO	1418	0.9641	1.745	4.5012	0.5150	715

0.2	4pH	1328	0.6512	0.658	6.7527	0.7675	758
	7pH	1560	1.0772	0.658	4.6694	0.4959	748
	10pH	1249	0.9560	0.584	4.6552	0.5257	127
0.4	DMSO	1512	0.9640	1.358	4.5012	0.5171	625
	4pH	1604	0.6511	0.658	6.7897	0.7697	614
	7pH	1410	1.0770	0.258	4.6703	0.4963	521
	10pH	1496	0.9557	0.367	4.6753	0.5270	410
0.6	DMSO	1508	0.9639	1.254	4.5621	0.5185	562
	4pH	1600	0.6509	0.654	6.8281	0.7720	541
	7pH	1408	1.0768	0.589	4.6844	0.4971	621
	10pH	1494	0.6509	0.458	4.6883	0.5279	714

Table.1. Acoustical parameters of red HE7B.

Conc %	**Solvents**	**U m / s**	**ρ Kg/m^3**	**η ×10^3 Nsm^{-2}**	**β ×10^{10} N^{-1}m^2**	**L$_f$ Å**	**π_i ×10^{-6} Pascal**
0.2	DMSO	1408	1.0760	1.498	4.7297	0.5301	501
	4pH	1513	0.9549	0.753	4.7317	0.4993	542
	7pH	1528	0.9630	0.732	6.8915	0.7760	569
	10pH	1438	0.6501	0.718	4.6338	0.5228	587
0.4	DMSO	1487	1.7057	1.514	4.7037	0.5305	514
	4pH	1501	0.5947	0.770	4.7421	0.5030	523

	7pH	1592	0.9626	0.748	6.9121	0.7771	563
	10pH	1497	0.6499	0.731	4.6419	0.5234	632
0.6	DMSO	1486	1.0755	1.559	4.7444	0.5314	841
	4pH	1398	0.9545	0.782	4.7474	0.5010	856
	7pH	1690	0.9623	0.757	6.9324	0.7784	459
	10pH	1495	0.6497	0.743	4.6558	0.5241	865

Table.2. Acoustical parameters of copper- red HE7B complex.

Conc %	**Solvents**	**U m / s**	**ρ Kg/m^3**	**$\eta \times 10^3$ Nsm^{-2}**	**$\beta \times 10^{10}$ $N^{-1}m^2$**	**L_f Å**	**$\pi_i \times 10^{-6}$ Pascal**
0.2	DMSO	1491	0.9630	1.865	4.6337	0.5227	859
	4pH	1594	0.6501	0.569	6.8915	0.7760	598
	7pH	1297	1.0760	0.856	4.7218	0.4993	856
	10pH	1399	0.9549	0.458	4.7297	0.5301	659
0.4	DMSO	1496	0.9626	1.895	4.6418	0.5234	569
	4pH	1592	0.6499	0.968	6.9121	0.7771	523
	7pH	1400	1.0757	0.389	4.7429	0.5000	521
	10pH	1288	0.9547	0.859	4.7307	0.5010	541
0.6	DMSO	1494	0.9623	1.965	4.6557	0.5241	652

	4pH	1690	0.6497	0.589	6.9328	0.7784	632
	7pH	1398	1.0753	0.548	4.7574	0.5010	641
	10pH	1486	0.9545	0.965	4.7444	0.5314	654

Table. 3. Acoustical parameter of lead- red HE7B complex.

Conc		**U**	**ρ**	**$\eta \times 10^3$**	**$\beta \times 10^{10}$**	**L_f**	**$\pi_i \times 10^{-6}$**
%	**Solvents**	**m / s**	**Kg/m^3**	**Nsm^{-2}**	**$N^{-1}m^2$**	**Å**	**Pascal**
0.2	DMSO	1402	1.0760	4.5012	4.7218	0.4937	741
	4pH	1518	0.9545	6.7527	4.7297	0.5019	458
	7pH	1237	0.9636	4.6694	4.6337	0.5278	856
	10pH	1654	0.6501	4.6552	6.8791	0.7607	589
0.4	DMSO	1400	1.0757	4.6014	4.7479	0.5036	458
	4pH	1788	0.9547	6.8791	4.7307	0.5059	589
	7pH	1596	0.9626	4.7138	4.6418	0.5342	459
	10pH	1492	0.6499	4.7160	6.9121	0.7714	561
0.6	DMSO	1398	1.0755	4.5621	4.7574	0.5103	254
	4pH	1286	0.9543	6.8281	4.7444	0.5420	652
	7pH	1494	0.9623	4.6844	4.6557	0.5415	405

	10pH	1390	0.6497	4.6883	6.9328	0.7845	506

Table.4. Acoustical parameters of nickel- red HE7B complex.

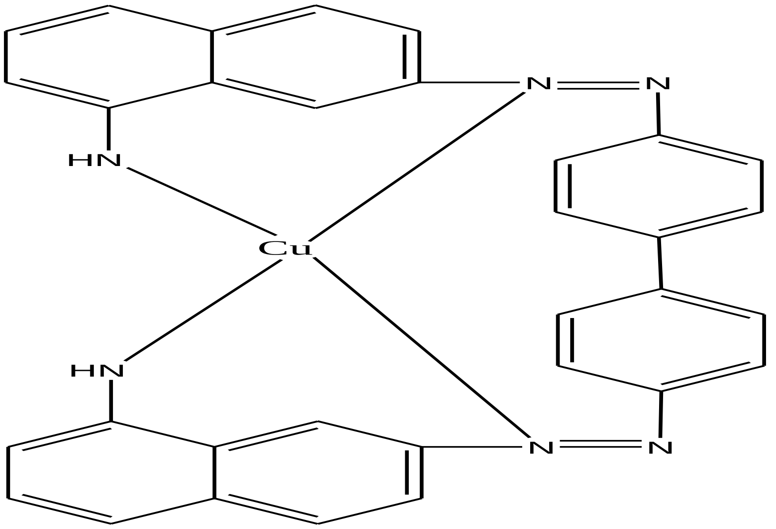

Fig.1. Red HE7B-copper complex

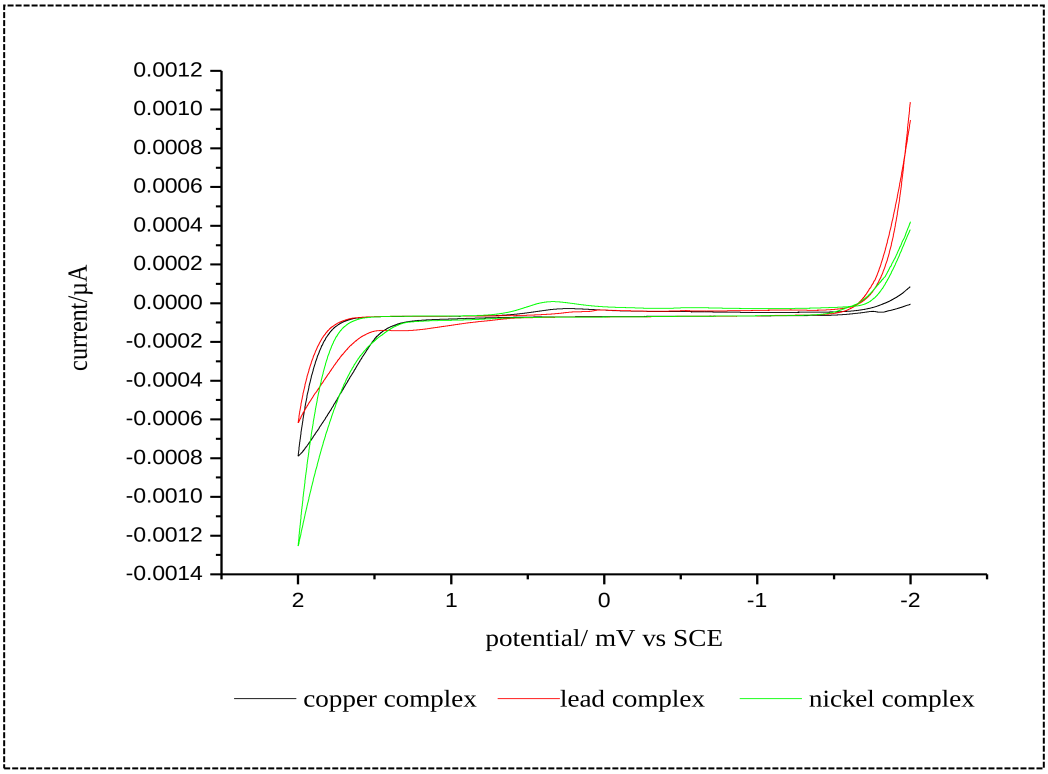

Fig.2. Cyclic voltammogram of red HE7B- Cu, Pb, Ni (II) complexes.

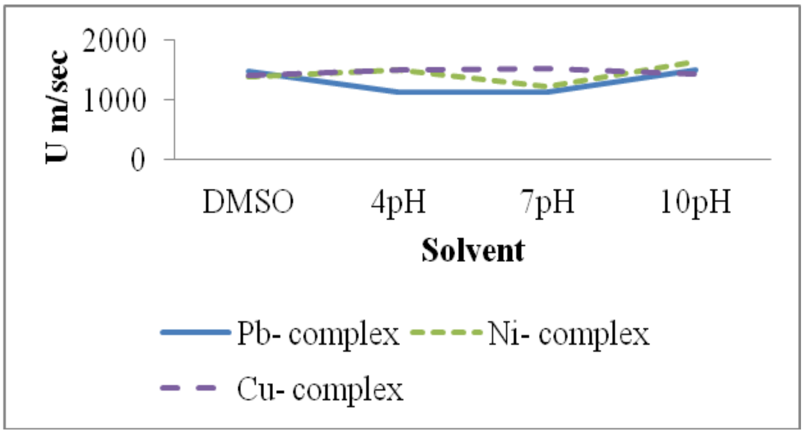

Fig.3. Ultrasonic velocity Vs solvents (DMSO and pH solutions) of M (Cu (II), Pb (II) and Ni (II))-complexes of red HE7B at 0.2 Concentration

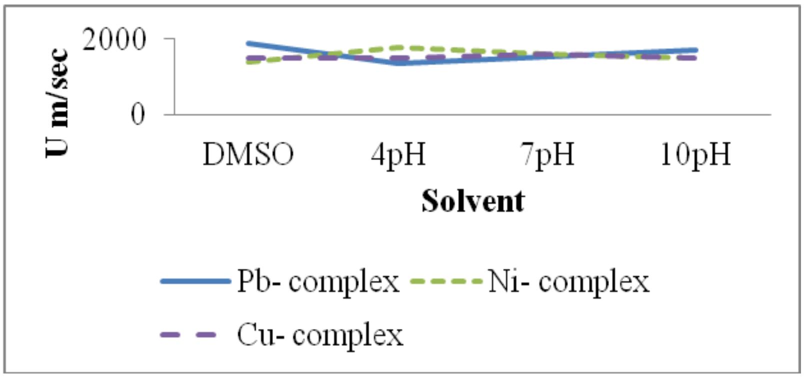

Fig.4. Ultrasonic velocity Vs solvents (DMSO and pH solutions) of M (Cu (II), Pb (II) and Ni (II))-complexes of red HE7B at 0.4 Concentration.

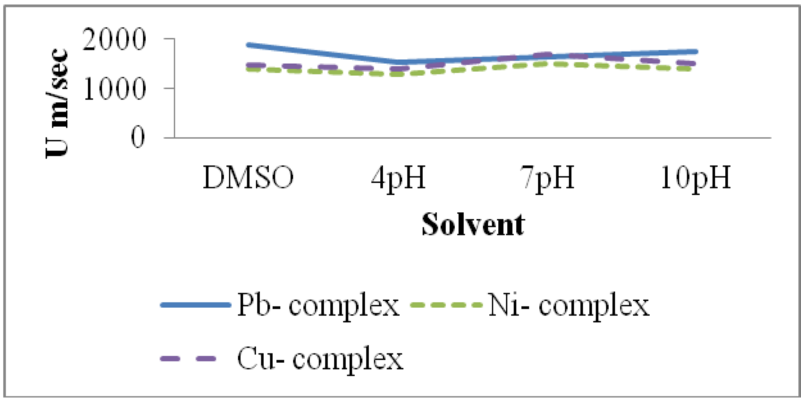

Fig.5. Ultrasonic velocity Vs solvents (DMSO and pH solutions) of M (Cu (II), Pb (II) and Ni (II))-complexes of red HE7B at 0.6 Concentration.

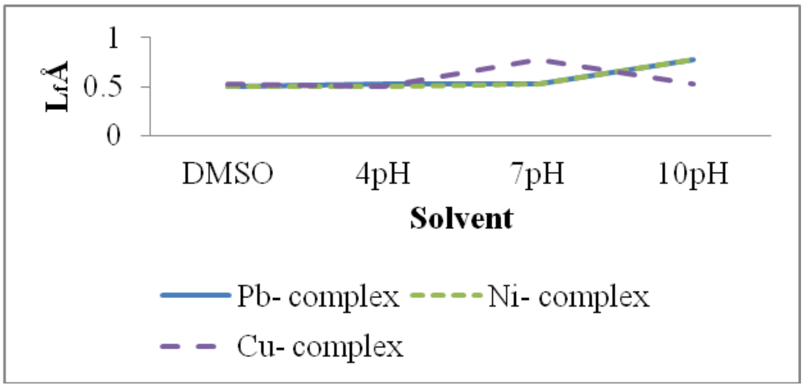

Fig.6. Adiabatic compressibility Vs solvents (DMSO and pH solutions) of M (Cu (II), Pb (II) and Ni (II))-complexes of HE7B at 0.2 Concentration.

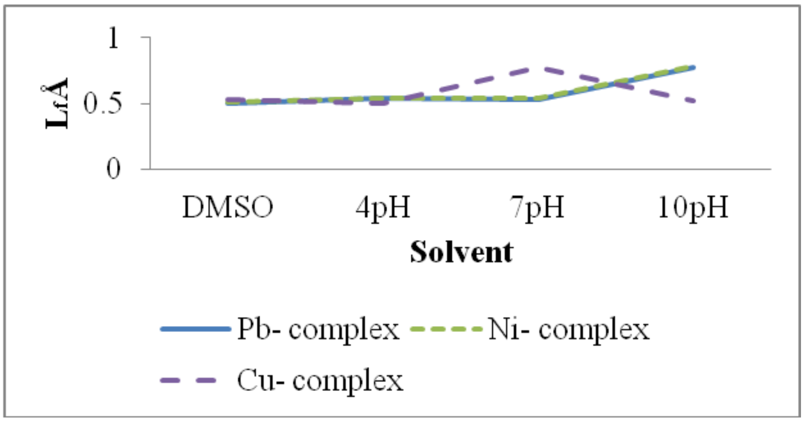

Fig.7. Adiabatic compressibility Vs solvents (DMSO and pH solutions) of M (Cu (II), Pb (II) and Ni (II))-complexes of red HE7B at 0.4 Concentration.

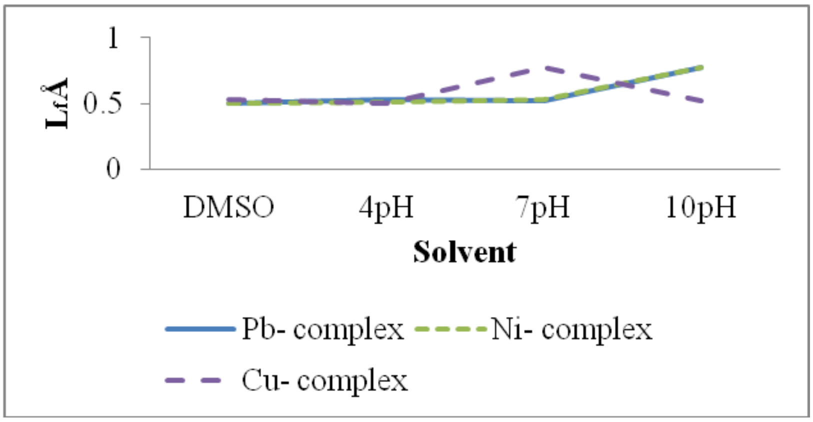

Fig.8. Adiabatic compressibility Vs solvents (DMSO and pH solutions) of M (Cu (II), Pb (II) and Ni (II))-complexes of HE7B at 0.6 Concentration.

CONCLUSIONS:

The cyclic voltammograms of Cu (II), Pb (II) and Ni (II) complexes of red HE7B showed a pair of peaks which are attributed to the electrode process that involves one electron where Cu^{3+}/ Cu^{2+} // Cu^{2+}/Cu^{3+}, Ni^{3+}/ Ni^{2+} // Ni^{2+}/Ni^{3+} copper and nickel respectively. The lead – red HE4B did not undergoes redox nature due to fast moving electron when open the ring of the complex. The adiabatic compressibility and intermolecular free length (Cu (II), Pb (II) and Ni (II)) decrease non-linearly with increase of concentration of metal complexes in all the solvents (DMSO and DMF). The decrease in compressibility at 4pH (copper and lead complexes) and 10pH (nickel complex) may be explained on the basic of close packing of the HE7B molecule in all the solvents (DMSO and DMF), finally resulting in an increase in ionic repulsion. So, internal pressure decreases with an increase in the concentration of metal complexes.

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