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Cyclic voltammetric and acoustical studies of some Cu (II), Ni (II) and Pb (II) complexes of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol at 303 k

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ABSTRACT

The cyclic voltammetric measurement and molecular interaction studies using ultrasonic technique of Cu(II),Ni(II) and Pb(II) complexes of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol using DMSO, were carried out at 303 K. The cyclic voltammetric were carried out at a stationary platinum electrode in DMSO with 0.1M tetrabutylammonium 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 behaviors were discussed.

Introduction

In recent years, ultrasonic technique has become a powerful tool for studying the molecular behavior of liquid mixtures [1-3]. This is because of its ability of characterizing physic-chemical behavior of liquid medium[4,5] .The measurement 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.

In this paper the electrochemical behavior of Cu (II), Ni (II) and Pb (II) complexes of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo] -naphthalene-1-ol 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 tetrabutylammonium 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.

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As can be shown in the (Fig.3) of the 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 -0.65 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 center of the complex.

Results and Discussion

The electrochemical behavior of the complexes Cu(II),Ni(II) and Pb(II) complexes of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol studied using cyclic voltammetry at a scan rate of the 0.1V/S after deaerating 10^{-3}M solution of the complexes in DMSO with tetrabutylammonium per chlorate (TBAP) as a supporting electrolyte.

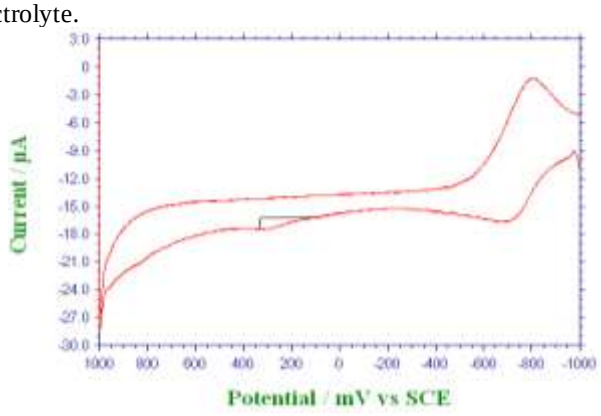

Fig. 1. Cyclic voltammogram of [Cu (II) complex of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol

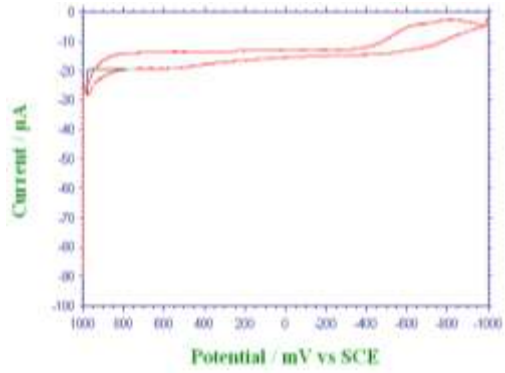

Fig.2.Cyclic voltammogram of [Pb (II) complex of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol

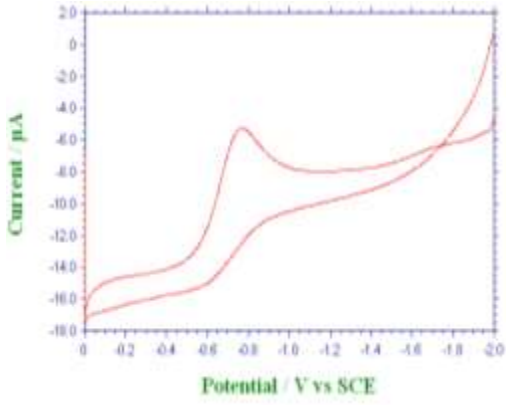

Fig.3.Cyclic voltammogram of [Ni (II) complex of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol

The cyclic voltammogram (Fig.1) of the complex shows that the oxidation and reduction of Cu (II) in the complex is characterized by a well defined redox peaks at -800 V (anodic) and -700 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 center of the complex.

In Fig.2, in addition to the Pb (II) peak, the obtained oxidation peak at the negative potential side indicated that the processes take place on the metal center of the complex (E=-600V). 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.

Based on these observations, the tetrahedral geometry is proposed for the complexes and a coordination number 4 is shown by M (II) (where M=Cu, Pb and Ni) in these complexes.

Using the measured values of ultrasonic velocity, density and viscosity of the solutions, other acoustical parameters are calculated and are shown in tables 1,2 and 3.Ultrasonic velocity is maximum at acidic pH (4) for [M (II) complex of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol and decreases from neutral pH to basic pH (10) in DMSO. (fig 5-13).

Ultrasonic velocity Vs solvents (DMSO and pH solutions) of M-complexes of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] solution in 0.2 % concentration at 303 K.

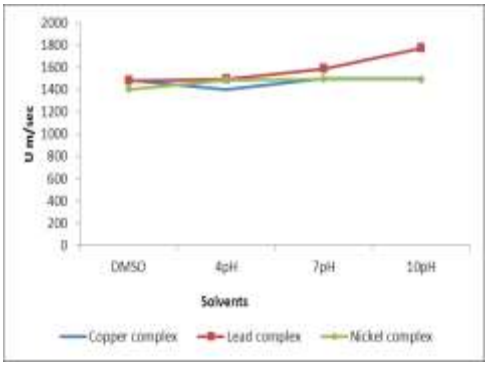

Fig.5. Ultrasonic velocity Vs solvents (DMSO and pH solutions) of M-complexes of8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] solution in 0.4 % concentration at 303 K

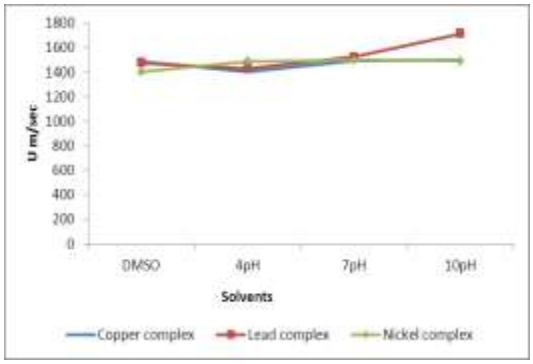

Fig.6. Ultrasonic velocity Vs solvents (DMSO and pH solutions) of M-complexes of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] solution in 0.6 % concentration at 303 K

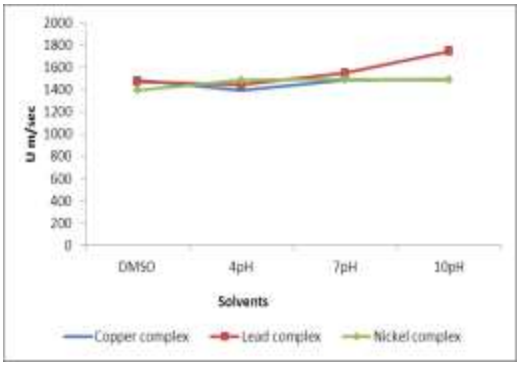

Fig.7. Adiabatic compressibility's Vssolvents (DMSO and pH solutions) of M-complexes of8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] solution in 0.2 % concentration at 303 K.

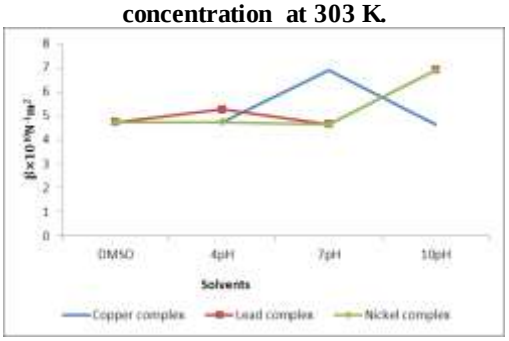

Fig.8. Adiabatic compressibility's Vssolvents (DMSO and pH solutions) of M-complexes of8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] solution in 0.4 % concentration at 303K

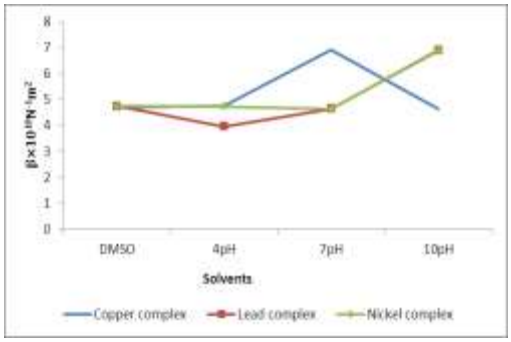

Fig.9. Adiabatic compressibility'sVssolvents (DMSO and pH solutions) of M-complexes of8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] solution in 0.6 % concentration at 303K

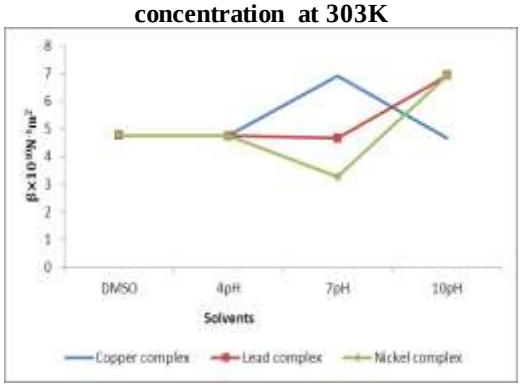

Fig.10.Intermolecular free length Vssolvents (DMSO and pH solutions) of M-complexes of8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] solution in 0.2 % concentration at 303K

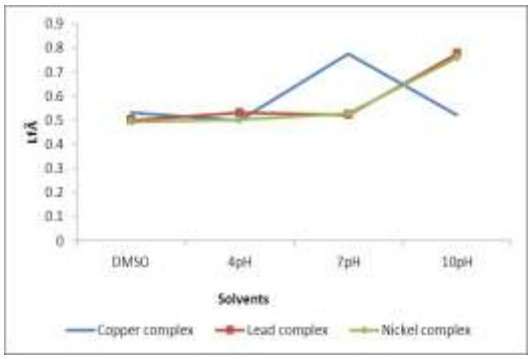

Fig.11. Intermolecular free length Vssolvents (DMSO and pH solutions) of M-complexes of8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] solution in 0.4 % concentration at 303K

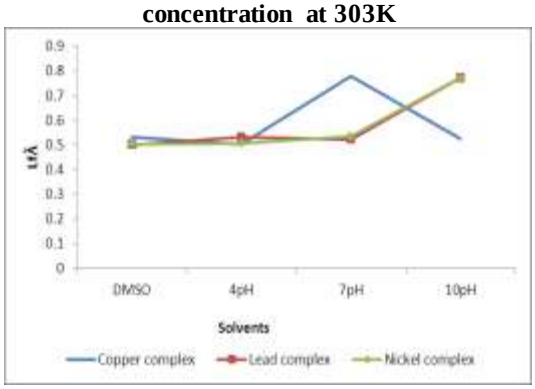

Fig.12. Intermolecular free length Vssolvents (DMSO and pH solutions) of M-complexes of8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] solution in 0.6 % concentration at 303K

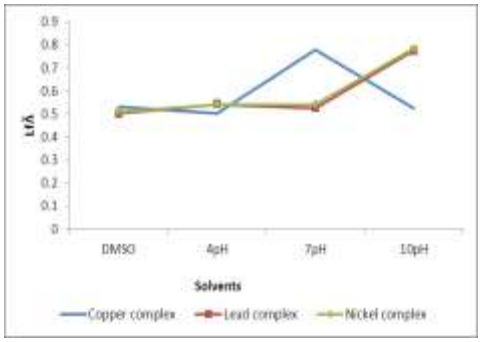

Fig.13. The increase in velocity near 4pH and 10 pH may be due to the fact that there may be strong interaction between the solvent and the solute. A similar effect has been observed by Ramrece Sanyal (2001).

From figs.8, to13 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 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] dyes by Rajagopalan and Sharma (2000). The decrease in compressibility at 4pH (copper complex) and 10pH (nickel complex) may be explained on the basic of close packing of the 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] molecule in all the solvent, finally resulting in an increase in ionic repulsion. So, internal pressure decreases with an increase in the concentration of M-complexes. The inter molecular free length decreases while specific acoustic impedance increases with an increase in concentrations indicating significant interaction between M-complexes and solvent molecules, which considerably affect the structural arrangements.

The salvation number decreases with increase in concentration. The value of salvation corresponds to the number of solvent molecules in the primary salvation sheath of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] molecule. The molecules in the salvation will be highly compressed and will be less compressible than those in the bulk of the solution when external pressure is applied.(Mehrotra and Kirti Tandon, 1990)

From the light of the above discussions, it may be concluded that the 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] dye have more bonding in 4pH with copper complex and 10pH lead and nickel complexes pneumonia than with the other three solvents. From the structure of the M-complexes and the solvent, the interaction is mainly between the O-H group of solvent and azo group of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol]. Although hydroxyl group is available in all the solvents, its configuration and conformation favour the interaction of O-H with azo group of the 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol].

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Table.1

Ultrasonic velocity and related acoustical parameters in the solution of [Cu (II) complex 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol]complex at 303 K.

Conc. %	Solvents	U m/s	ρ Kg/m^3	$\eta\times10^3$ Nsm^{-2}	$\beta\times10^{10}$ $N^{-1}m^2$	L_f Å	$\pi_i\times10^6$ Pascal	$Z_a\times10^6$ $Kgm^{-2}s^2$	S_n
0.2	DMSO	1488	1.0760	1.498	4.7297	0.5301	501	0.3554	84
	4pH	1403	0.9549	0.753	4.7317	0.4993	542	0.3774	74
	7pH	1498	0.9630	0.732	6.8915	0.7760	569	0.2428	45
	10pH	1498	0.6501	0.718	4.6338	0.5228	587	0.3605	45
0.4	DMSO	1487	1.7057	1.514	4.7037	0.5305	514	0.3551	86
	4pH	1401	0.5947	0.770	4.7421	0.5030	523	0.3766	95
	7pH	1492	0.9626	0.748	6.9121	0.7771	563	0.2428	93
	10pH	1497	0.6499	0.731	4.6419	0.5234	632	0.3601	56
0.6	DMSO	1486	1.0755	1.559	4.7444	0.5314	841	0.3545	85
	4pH	1398	0.9545	0.782	4.7474	0.5010	856	0.3761	65
	7pH	1490	0.9623	0.757	6.9324	0.7784	459	0.2421	57
	10pH	1495	0.6497	0.743	4.6558	0.5241	865	0.3569	84

Table.2

Ultrasonic velocity and related acoustical parameters in the solution of of [Pb (II) complex of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] complex at 303 K

Conc. %	Solvents	U m/s	ρ Kg/m^3	$\eta\times10^3$ Nsm^{-2}	$\beta\times10^{10}$ $N^{-1}m^2$	L_f Å	$\pi_i\times10^6$ Pascal	$Z_a\times10^6$ $Kgm^{-2}s^2$	S_n
0.2	DMSO	1481	0.9630	1.785	4.7281	0.4993	715	0.3377	47
	4pH	1497	0.6501	0.987	4.7297	0.5301	759	0.2428	46
	7pH	1589	1.0760	0.652	4.6373	0.5227	786	0.3600	46
	10pH	1776	0.5449	0.854	6.8915	0.7760	127	0.3554	25
0.4	DMSO	1474	0.9626	1.025	4.7429	0.5000	642	0.3617	63
	4pH	1430	0.6499	0.985	4.7307	0.5305	652	0.2435	58
	7pH	1523	1.0754	0.587	4.6418	0.5226	559	0.3766	86
	10pH	1714	0.9547	0.687	6.8991	0.7714	410	0.3551	44
0.6	DMSO	1474	0.9623	1.895	4.7574	0.5010	556	0.3595	54
	4pH	1444	0.6497	1.254	4.7444	0.5420	554	0.2421	25
	7pH	1550	1.0754	0.968	4.6575	0.5250	685	0.2761	58
	10pH	1745	0.9554	0.587	6.9328	0.7745	785	0.3545	48

Table.3

Ultrasonic velocity and related acoustical parameters in the solution of of [Ni (II) complex of8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol] complex at 303 K

Conc. %	Solvents	U m/s	ρ Kg/m^3	$\eta\times10^{3}$ Nsm^{-2}	$\beta\times10^{10}$ $N^{-1}m^{2}$	L_f Å	$\pi_i\times10^{6}$ Pascal	$Z_a\times10^{6}$ $Kgm^{-2}s^{-2}$	S_n
	DMSO	1402	1.0760	2.254	4.7218	0.4937	741	0.3773	85
0.2	4pH	1488	0.9545	0.965	4.7297	0.5019	458	0.3554	86
	7pH	1497	0.9636	0.547	4.6337	0.5278	856	0.3640	24
	10pH	1494	0.6501	0.854	6.8791	0.7607	589	0.2428	56
	DMSO	1400	1.0757	1.254	4.7479	0.5036	458	0.3766	45
0.4	4pH	1488	0.9547	0.685	4.7307	0.5059	589	0.3551	86
	7pH	1496	0.9626	0.874	4.6418	0.5342	459	0.3606	62
	10pH	1492	0.6499	0.985	6.9121	0.7714	561	0.2424	53
	DMSO	1398	1.0755	0.587	4.7574	0.5103	254	0.3761	52
0.6	4pH	1486	0.9543	0.584	4.7444	0.5420	652	0.3545	45
	7pH	1494	0.9623	0.598	3.2540	0.5415	405	0.3595	65
	10pH	1490	0.6497	0.874	6.9328	0.7845	506	0.2421	52