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Ultrasonics

Elixir Ultrasonics 46 (2012) 8268-8272

ISSN: 2229-712X

Electrochemical studies of Marine Dyes with some Cu (ii), Ni (ii), Zn(ii) and Pb (ii) metal complexes of 4-amino-3, 6-bis [[4-[[4-chloro-6-[(3-Sulfophenyl) Amino]-1,3,5-Triazin-2-yl]Amino]-2-Sulfophenyl]Azo]-5-hydroxy-2,7-Naphthalenedisulfonic acid hexasodium compound

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ARTICLE INFO

Article history:

Received: 23 February 2012;

Received in revised form:

15 April 2012;

Accepted: 9 May 2012;

Keywords

Cyclic voltammetric technique,
Ultrasonic technique,
Acoustical parameters and dyes with
Metal-coordination.

ABSTRACT

The cyclic voltammetric measurement and molecular interaction studies using ultrasonic technique of Cu(II),Ni(II), Zn(II) and Pb(II) complexes of 4-Amino-3, 6-Bis [[4-[[4-Chloro-6-[(3-Sulfophenyl) Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic acid hexasodium compound using DMSO, have been studied at 303 K. The cyclic voltammetric were carried out using 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 these properties the parameters have been studied the nature and strength of the interactions in these complexes and oxidation, reduction behaviors were discussed.

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Introduction

The modern technique of the present studies, namely ultrasonic technique of adiabatic compressibility study have 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 the ultrasonic velocity have been adequately employed in understanding the molecular interactions in the 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[13-16]. In this present investigation the electrochemical behavior of Cu(II),Ni(II) , Zn(II) and Pb(II) complexes of 4-Amino-3, 6-Bis [[4-[[4-Chloro-6-[(3-Sulfophenyl) Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic acid hexasodium compound were investigated. Recently the present electrochemical studies of this complexes work have never been reported else were.

Experimental

The ultrasonic velocity has been measured at 303 K using a crystal interferometer with a high degree of accuracy operating at a frequency of 2 MHz the density were measured at 303 K using specific gravity bottle by the standard procedure. The electrochemical measurements were performed with a Princeton Applied Research model -173 potentiostat, a universal programmer model were175 and an X-Y recorder, Model RE 0074. One compartment electrochemical cell were 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.

As shown in the (Fig.2) 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 Cu(II),Ni(II) , Zn(II) and Pb(II) complexes of 4-Amino-3, 6-Bis [[4-[[4-Chloro-6-[(3-Sulfophenyl) Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic acid hexasodium compound 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.

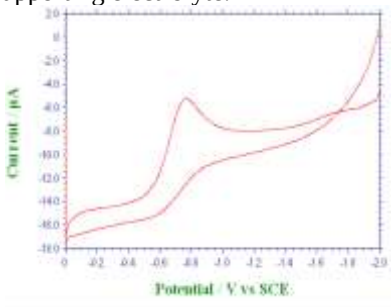

Fig.1. Cyclic voltammogram of Zn (II) complex of 4-Amino-3, 6-Bis [[4-[[4-Chloro-6-[(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic acid hexasodium compound

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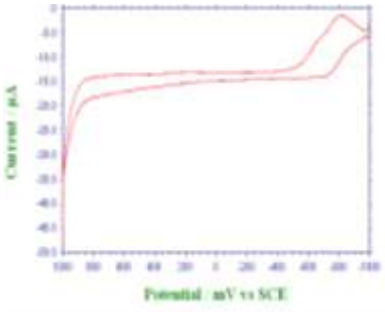

Fig. 2.Cyclic voltammogram of Cu (II) complex of 4-Amino-3, 6-Bis [[4-[[4-Chloro-6-[(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic acid hexasodium compound

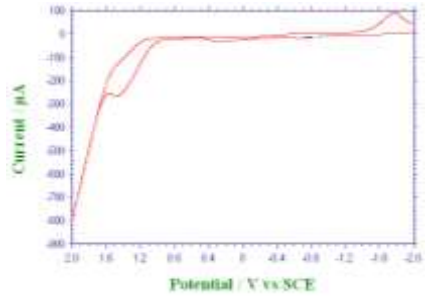

Fig.3.Cyclic voltammogram of Pb (II) complex of 4-Amino-3, 6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium complexes

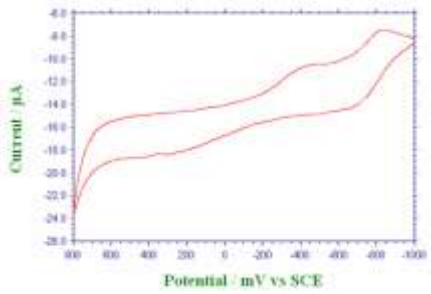

Fig.4.Cyclic voltammogram of Ni (II) complex of 4-Amino-3, 6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic acid hexasodium complexes

The cyclic voltammogram (Fig.1) of the complex shows that the oxidation and reduction of Cu (II) in the complex were 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) the peak obtained shows the 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 Zn and Ni) in these complexes.

Table.1

Ultrasonic velocity and related acoustical parameters in the solution of [Zn (II) complex of 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium complexes at 303 K.

Using the measured values of ultrasonic velocity, density and viscosity of the solutions, other acoustical parameters were calculated and are shown in Tables 1,2,3 and 4.Ultrasonic velocity is maximum at acidic P^H-4.8 for [M (II) complex of 8-[2-Methoxy-5-(propane-1-sulfonyl)-phenylazo]-naphthalene-1-ol and decreases from neutral P^H to basic P^H-10.5 in DMSO.(Fig5-13).

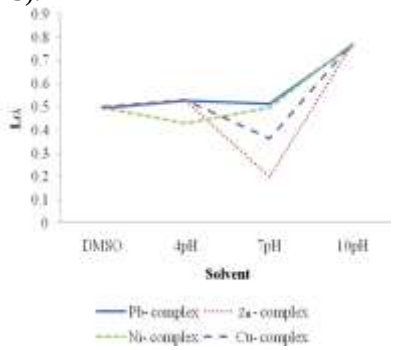

Fig.5. Ultrasonic velocity Vs solvents (DMSO and pH solutions) of M-complexes complexes of 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic acid hexasodium solution in 0.2 % concentration at 303 K.

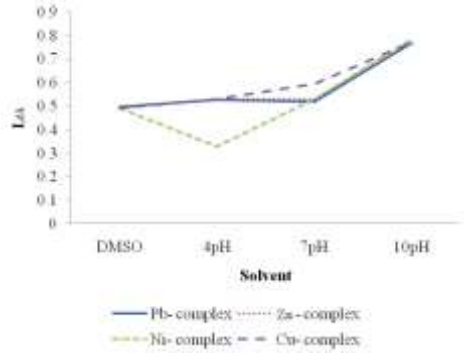

Fig.6. Ultrasonic velocity Vs solvents (DMSO and pH solutions) of M-complexes 4-Amino-3, 6-

Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium solution in 0.4 % concentration at 303 K.

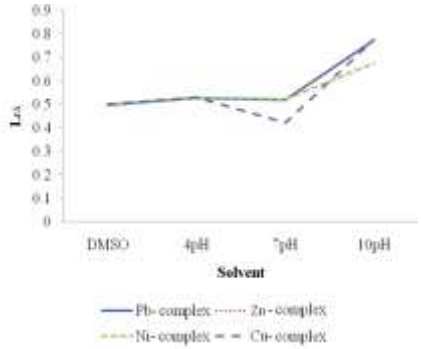

Fig.7. Ultrasonic velocity Vs solvents (DMSO and pH solutions) of M-complexes 4-Amino-3, 6-

Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic acid hexasodium solution in 0.6 % concentration at 303 K.

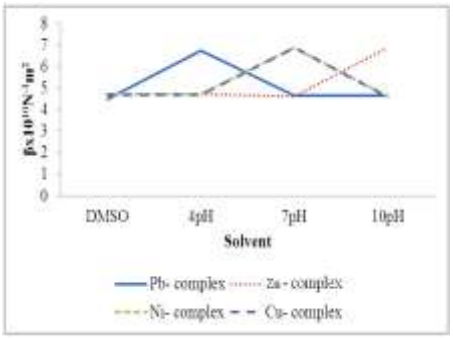

Fig.8. Adiabatic compressibility's Vssolvents (DMSO and pH solutions) of M-complexes 4-

Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium solution in0.2 % concentration at 303 K.

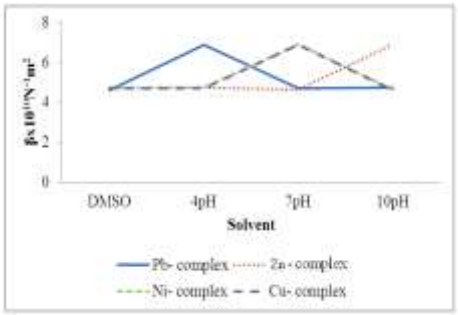

Fig.9. Adiabatic compressibility's Vssolvents (DMSO and pH solutions) of M-complexes 4-

Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium solution in 0.4 % concentration at 303K

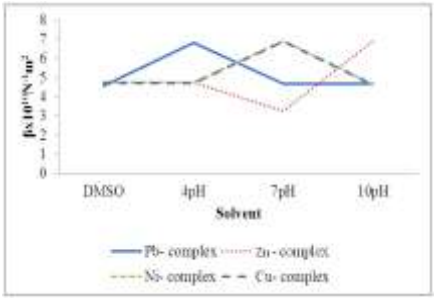

Fig.10. Adiabatic compressibility's Vssolvents (DMSO and pH solutions) of M-complexes of 4-

Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium solution in 0.6 % concentration at 303K

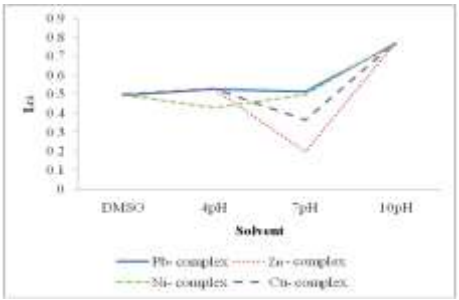

Fig.11. Intermolecular free length Vssolvents (DMSO and pH solutions) of M-complexes of 4-

Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium solution in0.2 % concentration at 303K

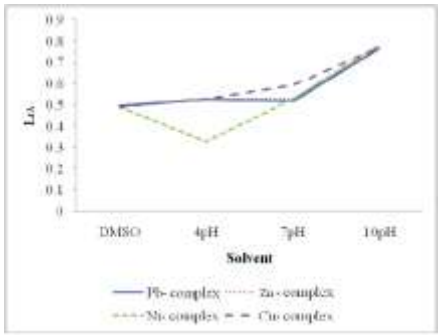

Fig.12. Intermolecular free length Vssolvents (DMSO and pH solutions) of M-complexes of 4-

Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium solution in0.4 % concentration at 303K

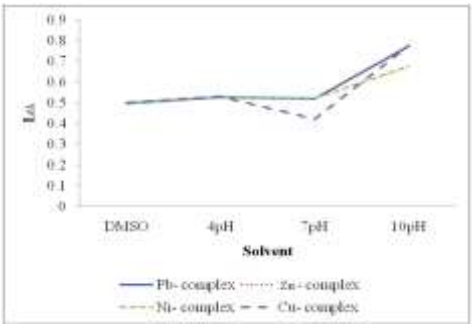

Fig.13. Intermolecular free length Vssolvents (DMSO and pH solutions) of M-complexes of 4-

Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl]Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium solution in 0.6 % concentration at 303K

The velocities have been increased near to P^H 4.8 and P^H 10.8 it may be due to the fact that there may be strong interaction between the solvent and the solute. Adiabatic compressibility's Solvents (DMSO and pH solutions) of M-complexes of with 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium solution in different percentage of concentration(2%,4% and 6%) at 303K up to the intermolecular free length Solvents (DMSO and P^H solutions) of M-complexes of 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium solution in different percentage of concentration(2%,4% and 6%) at 303K. The adiabatic compressibility and intermolecular free length decrease non-linearly with increase of concentration of metal complexes in all the solvents. The decrease indent shows that may be more pronounced at acidic pH for all metal complexes and at basic pH for pneumonia 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium. The decrease in compressibility at P^H 4.8 (copper complex) and P^H 10.8 (nickel complex) may be explained that the basic of close packing of the 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1,

3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium 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 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium 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.

Conclusion

The 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium dye have more bonding in P^H 4.8 with copper complex and P^H10.8 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 4-Amino-3, 6-Bis [[4-[[4-Chloro-6-[(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium. Although hydroxyl group is available in all the solvents, its configuration and conformation favor to the interaction of O-H with azo group of the 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium.

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Table.1Ultrasonic velocity and related acoustical parameters in the solution of [Zn (II) complex of 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium complexes 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	1469	0.9637	1.785	4.6991	0.4972	857	0.3768	74
	4pH	1451	0.6508	0.987	4.6950	0.5283	965	0.3566	85
	7pH	1324	1.0764	0.652	4.5810	0.1974	851	0.3626	94
	10pH	1758	0.9555	0.854	6.8560	0.7752	514	0.2453	61
0.4	DMSO	1469	0.9635	1.025	4.6990	0.4909	547	0.3738	85
	4pH	1470	0.6506	0.985	4.7019	0.5278	596	0.3526	46
	7pH	1320	1.0763	0.587	4.5881	0.5295	854	0.3623	95
	10pH	1775	0.9554	0.685	6.8678	0.7715	524	0.2433	35
0.6	DMSO	1471	0.9633	1.895	4.7131	0.4985	856	0.3777	48
	4pH	1371	0.6504	1.254	4.7166	0.5278	951	0.3575	75
	7pH	1500	1.0762	0.968	4.6017	0.5201	752	0.3671	98
	10pH	1759	0.9551	0.587	6.9187	0.7759	741	0.2413	53

Table.2

Ultrasonic velocity and related acoustical parameters in the solution of [Cu (II) complex of 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium complexes 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	1297	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	1376	0.5449	0.854	6.8915	0.7760	127	0.3554	25
0.4	DMSO	1469	0.9635	1.025	4.6990	0.4909	547	0.3738	85
	4pH	1270	0.6506	0.985	4.7019	0.5278	596	0.3526	46
	7pH	1520	1.0763	0.587	4.5881	0.5955	854	0.3623	95
	10pH	1375	0.9554	0.685	6.8678	0.7715	524	0.2433	35
0.6	DMSO	1471	0.9633	1.895	4.7131	0.4985	856	0.3777	48
	4pH	1371	0.6504	1.254	4.7166	0.5278	951	0.3575	75
	7pH	1500	1.0762	0.968	4.6017	0.4201	752	0.3671	98
	10pH	1659	0.9551	0.587	6.9187	0.7759	741	0.2413	53

Table.3

Ultrasonic velocity and related acoustical parameters in the solution of [Pb (II) complex of 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium complexes 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	1466	0.9641	1.085	4.6694	0.4959	458	0.3799	54
	4pH	1465	0.6512	0.865	4.6552	0.5297	456	0.3584	86
	7pH	1515	1.0770	0.547	4.5012	0.5150	481	0.3658	95
	10pH	1767	0.9565	0.468	6.7527	0.7675	463	0.2455	75
0.4	DMSO	1467	0.9640	1.549	4.6703	0.4963	456	0.3796	65
	4pH	1467	0.6512	0.598	4.6753	0.5270	658	0.3575	85
	7pH	1517	1.0776	0.658	4.5375	0.5171	416	0.3643	24
	10pH	1769	0.9556	0.547	6.7897	0.7697	562	0.2448	96
0.6	DMSO	1468	0.9639	1.458	4.6844	0.4971	421	0.3790	87
	4pH	1383	0.6509	0.562	4.6863	0.5276	432	0.3569	95
	7pH	1518	1.0768	0.485	4.5621	0.5185	352	0.3633	91
	10pH	1770	0.9556	0.854	6.8281	0.7720	568	0.2440	67

Table. 4

Ultrasonic velocity and related acoustical parameters in the solution of of [Ni (II) complex of 4-Amino-3, 6-Bis [[4-[[4-Chloro-6- [(3-Sulfophenyl) Amino]-1, 3, 5-Triazin-2-Yl] Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic acid hexasodium 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	1469	0.9637	1.785	4.6991	0.4972	857	0.3768	74
	4pH	1451	0.6508	0.987	4.6950	0.4283	965	0.3566	85
	7pH	1524	1.0764	0.652	4.5810	0.4974	851	0.3626	94
	10pH	1658	0.9555	0.854	6.8560	0.7752	514	0.2453	61
0.4	DMSO	1469	0.9635	1.025	4.6990	0.4909	547	0.3738	85
	4pH	1370	0.6506	0.985	4.7019	0.3278	596	0.3526	46
	7pH	1520	1.0763	0.587	4.5881	0.5295	854	0.3623	95
	10pH	1775	0.9554	0.685	6.8678	0.7865	524	0.2433	35
0.6	DMSO	1471	0.9633	1.895	4.7131	0.4985	856	0.3777	48
	4pH	1371	0.6504	1.254	3.7166	0.5278	951	0.3575	75
	7pH	1500	1.0762	0.968	4.6017	0.5201	752	0.3671	98
	10pH	1759	0.9551	0.587	3.9187	0.6759	741	0.2413	53