CONDUCTOMETRIC STUDIES AND EVALUATION OF THERMODYNAMIC PARAMETERS IN MICELLAR MEDIUM FOR COMPLEXES OF HO(III)-INDOLE DERIVATIVES

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ABSTRACT

Conductometric studies of Nitrogen and Oxygen containing ligands of Indole derivative (viz :1*H*-indole -3-carboxylic acid,1-(1*H*-indole-3-yl) ethanone, 1*H*-indole-3-carbaldehyde, 2-(1*H*-indole-3-yl)ethanoic acid, 4-(1*H*-indole-3-yl)butanoic acid with Holmium(III)-complexes have been analyzed in alcohol+water and micellar medium [BRIJ35, CTAB, SDS]. Conductometric titration curves outcomes are association constant K_A, Gibbs free energy of association ΔG_A, formation constant or stability constant K_f as $\log K_f$ and Gibbs free energy of formation ΔG_f. The formation of different stoichiometric complexes 1:1, 1:2, 1:3 [M:L] ratio are obtained as inflammation point in the plot of molar conductance Λ_m (S cm^2 mol^{-1}) and ligand/metal $[L]_t$ / $[M]_t$ ratio of Holmium(III)-with Indole derivative I3CA, 3ATI, I3CD, 2IEA, 4IBA at 298 K temperature in different greener micellar systems. Stability of 1:1, 1:2, 1:3 [M:L] metal ligand complexes have been calculated in term of formation constant as $\log K_f$ and ΔG_f thermodynamic parameter. On increasing the metal ligand ratio magnitude of $\log K_f$ and ΔG_f shows a different behavior in micellar as well as in non-micellar medium. Strengthening of Ho(III) with indole derivatives complexes are observed somewhat different on alteration of micellar systems.

KEYWORDS: Micellar Medium, Gibbs free energy, Formation Constant, Stoichiometric Complexes, Thermodynamic Parameters.

1. INTRODUCTION

In recent years, studies of the metal-ligand complexes, different methods like conductometric titration, voltammetry, polarography, colorimetry, spectrophotometry, potentiometry and fluorescence spectroscopy techniques are using for investigation. Among these techniques of investigation, conductometric titration method is highly sensitive, easy handling, eco-friendly, low-cost requirement and uncomplicated instrumental experimental technique [1-6]. Basic skeleton of Indole derivatives has 10 π electron and aromatic heterocyclic systems having benzene ring and N-based pyrrole ring fused at α, β position by sharing 2π electrons [7]. Now a days, Indole derivatives nucleus have importance in the field of cell biology, pharmacological activity, studies of drug discovery and treatment of human health disorders. 2-(1*H*-indole-3-yl)ethanoic acid derivatives are used for potential activity against inflammation, treatment of rheumatoid arthritis (Indomethacin), analgesic agents, relief in cluster headache, treatment of alcoholism and pain[8-9]. For targeted cancer therapy 6-chloro substituted indole-3-acetic acid prodrugs are used, as it has high cytotoxicity upon horseradish peroxidase activation (HRP) [10]. Antimicrobial activity in 3-acetyl indole and pyrazine have been reported against bacterial strains [11]. 6-bromo derivative of 1*H*-indole-3-carbaldehyde are used in cosmetics due to antioxidant activity, anticancer and anti-inflammatory activity [12]. Spirocyclization of indoles achieved successfully at 2 or 3-position with inorganic catalytic and organic catalytic systems for medicinal and pharmacological importance due to high rigidity and 3-D geometries [13].

Use of Holmium in medical field for diagnosis of disease and treatment, industries, glass and ceramics, petroleum and analytical fields are emerging fields. For detection of Ho(III) ion in human serum, holmium alloys and environmental water samples, multilayer carbon nanotubes are used which have Ho(III) carbon paste sensors. pH free response and good selectivity are the advantages of these Ho (III) carbon paste sensors. These sensors produce fast response and good selectivity with the Ho containing samples [14]. For clinical application, Holmium laser lithotripsy are used for stone fragmentation or dusting, depending upon the combination of 'pulse energy' and 'pulse frequency' in ureteroscopy. To reduce stone retropulsion, long 'pulse width' mode is used [15]. For treatment of cancer, radioactivity induced in ^{165}Ho to produce ^{166}Ho just before applying on the cancer cells due to short half-life period of ^{166}Ho. By emission of β^-particles, recently produce radioactive ^{166}Ho, DNA of cancer cells are fragmented or destroyed to cure the cancer disease [16].

In lanthanide, 4f subshell electron exhibit lanthanide contraction, more attracted by nucleus, deeply situated than 5d, and are shielded by 5s and 5p subshell electrons. Hence, lanthanide show less interaction compare to transition metals with ligands as these have shielded, 4f lower energy orbitals. Smaller size lanthanide has more polarization power to its neighbor element, as radii decrease 0.0152 Å between two neighbor lanthanides [17]. Metal-ligand interaction in lanthanide have been reported in previous literature. Diversity in coordination types and properties are exhibited by O- and N- donor multifunction ligand [18]. Interaction study of lanthanides with oxalate, imidazole dicarboxylate ion construct 2-D structure in which bond length Ln-O, Ln-N reduced on moving towards heavier lanthanides [19]. Study of thermodynamic parameters for complexation of Calix[4]pyrrole with Holmium, justify that 1:2 metal-ligand complex between these two moieties takes place in non-aqueous medium. Interaction is observed between active site of hard N-donor atom and hard lanthanide cation [20]. 4f oblate electron density of Ho (III) are affected by ligand field environment. In high angular momentum projection, more stabilization of energy occurs when ligand N-heterocyclic pyrazole and carbene approaches towards metal ion in axial position [21]. Lanthanide Ho atom coordinate with organic compounds by coordination bond. Terephthalic acid as linker and Ho as central atom of complex form cloverleaf-shaped two chiral phases as Ho-TPA complex, in which bonding environment, their stability, and charge transfer are delineated by density functional theory and tunneling microscopy [22].

In this Conductometric studies, Holmium (III) with indole derivatives 1*H*-indole-3-carboxylic acid(I3CA), 1-(1*H*-indole-3-yl)ethanone(3ATI), 1*H*-indole-3-carbaldehyde(I3CD), 2-(1*H*-indole-3-yl)ethanoic acid(2IEA), 4-(1*H*-indole-3-yl)butanoic acid(4IBA)have been investigated in different thermodynamic parameters in greener micellar medium CTAB (Cetyl trimethyl ammonium bromide), BRIJ35 (Polyethylene glycol monododecyl ether), SDS (Sodium dodecyl sulphate) solvent systems. This existing Conductometric study are focused on metal-ligand interaction and analysis of thermodynamic parameter related to complexes of Ho (III) with Indole derivative as N- and O- donor ligands. Micellar surfactants are environmentally friendly having low toxic impacts on the environment [23]. No earlier conductometric studies of Ho (III) cation have been reported with indole derivatives I3CA, 3ATI, I3CD, 2IEA, 4IBA in non micellar as well as in nonionic micellar surfactant BRIJ35, anionic micellar surfactant SDS and cationic micellar surfactant CTAB system.

Aim of this conductometric study to know metal-ligand interaction, stoichiometry ratio of metal-ligand complexes, spontaneously formation of complexes and stability of metal-ligand complexes through thermodynamic parameters.

2. EXPERIMENTAL SECTION

2.1 Preparation of Solutions

Holmium(III)chloride of central drug house (P) Ltd. and Indole derivatives ligands I3CA, 3ATI, I3CD, 2IEA, 4IBA of Qualigens, Thermo fisher scientific, India Pvt Ltd was used. Standard solution of Holmium(III)chloride and ligands were prepared of 0.05 M concentration. Solvent ethanol of AR grade 99.9% purity manufacturer by Changshu Hongsheng fine chemical Co. Ltd. Jiangsu, was purchased. BRIJ35, SDS and CTAB manufactured by Loba Chemia Pvt. Ltd. Mumbai, India, were used in conductometric titration. For the measurement of conductivity of metal and ligands system, at constant temperature 298 K, highly sensitive DDS-12 DW conductivity meter has been used which has a cell constant 1.0 cm^{-1}. In this experiment, metal solutions having 1×10^{-3} M concentration and ligands I3CA, 3ATI, I3CD, 2IEA, 4IBA having concentration 1×10^{-2} M were prepared in ethanol+water and BRIJ35, SDS, CTAB greener solvent systems. Double distilled and deionized water having conductivity less than 5 µS was used during the entire experiment.

2.2 Procedure for conductometric method

Ho(III) metal ion solution conductometrically titrated with different Indole derivatives I3CA, 3ATI, I3CD, 2IEA, 4IBA in greener micellar BRIJ35, CTAB , SDS and non-micellar alcohol+water medium. For titration Ho(III)metal ion solution(25 mL of 1×10^{-3} M) put in the thermostat and conductivity was measured by conductivity meter. Ligands solution (1×10^{-2} M) I3CA, 3ATI, I3CD, 2IEA, 4IBA in different mediums added to metal solution by 0.4 mL increment. The specific conductance of different solutions measured experimentally by conductivity meter which was converted into corrected conductance using (V+v)/V as dilution occurs by adding the ligand solution into the metal solution [24-25]. Corrected conductance converted into the molar conductance Λ_m [26]. By extrapolating of the graph between molar conductance Λ_m and $C_m^{1/2}$ to zero concentration, limiting molar conductance Λ_o was obtained [27]. Plot between the molar conductance Λ_m and ligand/metal ratio $[L]_t/[M]_t$ has been drawn for ligands I3CA, 3ATI, I3CD, 2IEA and 4IBA Indole derivatives in different greener solvent systems.

2.3 Calculations of Association Constant K_A and Gibbs Free Energy of Association G_A

For calculation of association constant equation (1) used [28-30].

$$K_A = \frac{\Lambda_0^2\ (\Lambda o - \Lambda)}{4\ C_m^2 \gamma_\pm^2 \Lambda^3 S\ (Z)^2} \text{------------------------------}(1)$$

Λ_o = Limiting molar conductance
Λ = observed molar conductance
C_m= concentration of metal
$\gamma_\pm$= mean ionic activity coefficient
s(z)= fuoss-shedlovsky factor

For calculation of Gibbs free energy of Association G_A apply equation (2) for non-micellar and micellar system

$$\Delta G_A = -RT\ ln\ K_A \text{--}(2)$$

2.4 Calculations of Formation Constant K_f and Gibbs Free Energy of Formation ΔG_f

Formation of metal -ligand binding between Holmium(III) ion and Indole derivative can be shown as

$$M^+ + L \rightleftharpoons ML^+$$

The formation constant K_f or stability constant represented in equation (3) for above equilibrium [31-32]

$$K_f = \frac{[ML^+]}{[M^+][L]}$$

$$K_f = \frac{\Lambda_{M+} - \Lambda}{\Lambda - \Lambda_{ML}\quad [L]} \text{----------------------------------}(3)$$

Λ_{M+} = Molar conductivity of metal
Λ_{ML} = Molar conductivity of complexed cation solution
[L] = Concentration of ligand
Λ = observed molar conductance

Gibbs free energy of Formation was calculated by equation (4) for metal and ligand complex in non-micellar and micellar system

$$\Delta G_f = -RT\, ln\, K_f \text{------------------------------------} (4)$$

3. RESULT AND DISCUSSION

Plot of Ho(III) with indole derivative I3CA, 3ATI, I3CD, 2IEA, 4IBA between molar conductance Λ_m in non micellar (alcohol+water) medium and in micellar medium (BRIJ35, CTAB, SDS) and the ligand to metal $[L]_t / [M]_t$, total concentration ratio at 298 K are obtained in different lines with sharp inflammation point, illustrating the formation of 1:1, 1:2, 1:3 [M:L] ratio as shown in different figures 1-10. To obtained association constant K_A and Gibbs free energy of association ΔG_A, the value of limiting molar conductance Λ_o was obtained by the extrapolation of graph between molar conductance Λ_m and $C_m^{1/2}$ to zero concentration [26-27]. By conductometric study, Association constant K_A and Gibbs free energy of Association ΔG_A of Ho(III) with indole derivatives I3CA, 3ATI, I3CD, 2IEA, 4IBA in non-micellar alcohol+water medium and micellar medium (BRIJ35, CTAB, SDS) mediums have been reported in Table 1-2.

The magnitude of thermodynamic parameters, association constant K_A and Gibbs free energy of association ΔG_A of Ho(III)-I3CA, Ho(III)-3ATI, Ho(III)-I3CD are observed higher in alcohol+water medium as compared to nonionic surfactant BRIJ35 medium for these three complex systems while the value of K_A and ΔG_A for Ho(III)-2IEA and Ho(III)-4IBA are observed higher in cationic surfactant CTAB and anionic surfactant SDS medium as compare to alcohol+water medium. From Table 1-2, It inferred that as the concentration of Holmium $C_{m[Metal]}$ decreases, thermodynamic parameters K_A and ΔG_A decreases in the Ho(III)-I3CA, Ho(III)-3ATI, Ho(III)-I3CD, Ho(III)-2IEA and Ho(III)-4IBA systems in both, non micellar alcohol+water as well as in micellar BRIJ35, CTAB, SDS medium.

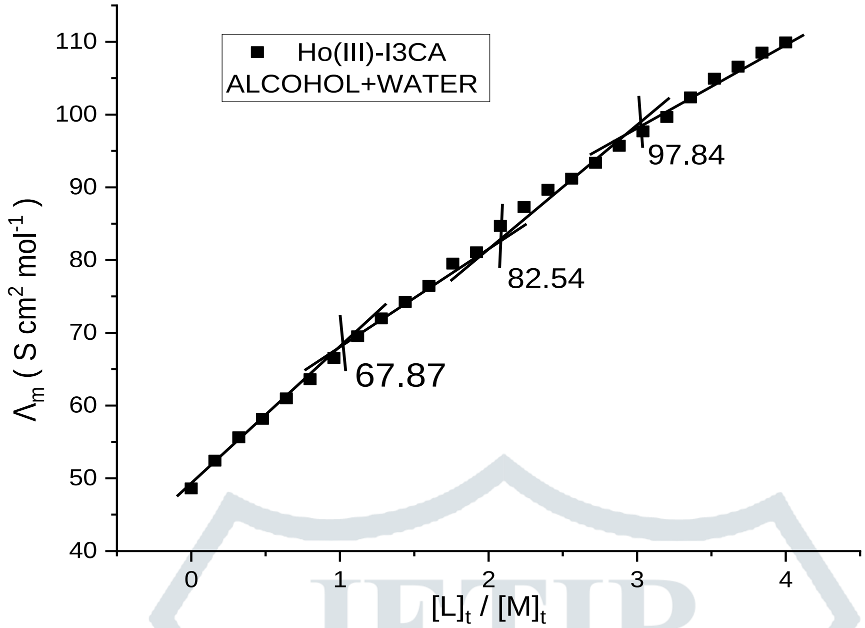

Figure-1. Molar conductance Λ_m (S cm^2 mol^{-1}) with 1*H*-indole-3-carboxylic acid (I3CA) Holmium(III), $[L]_t / [M]_t$ graph in non-micellar medium at 298 K temperature.

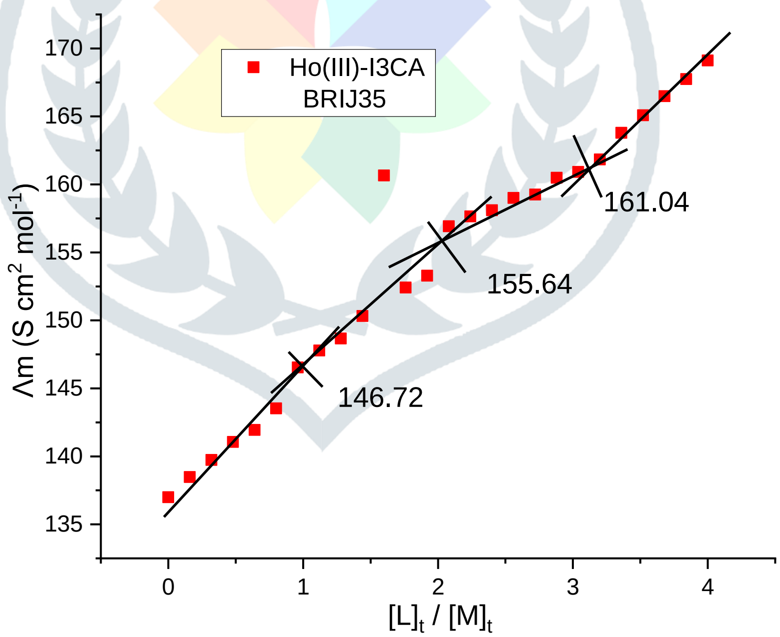

Figure-2. Molar conductance Λ_m (S cm^2 mol^{-1}) with 1*H*-indole-3-carboxylic acid (I3CA) Holmium(III), $[L]_t / [M]_t$ graph in micellar medium (BRIJ35) at 298 K temperature.

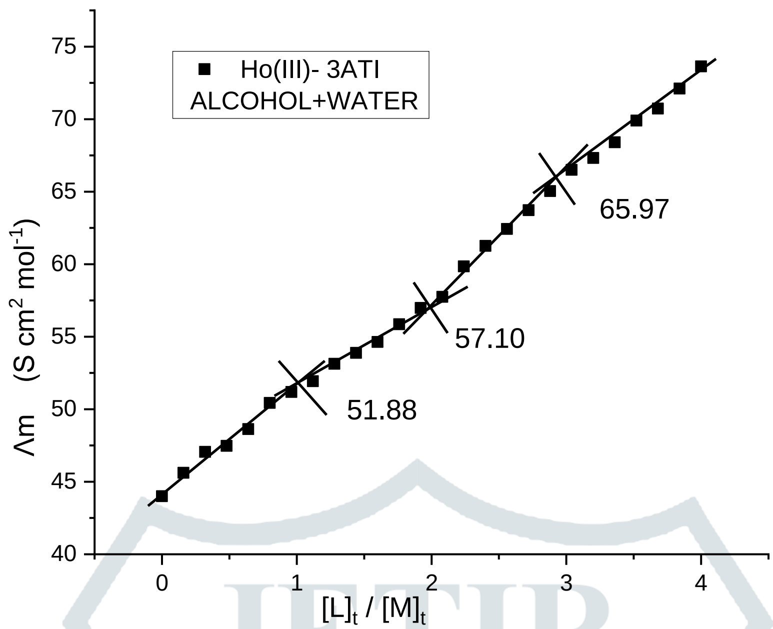

Figure-3. Molar conductance Λm (S cm2 mol-1) with 1-(1H-indole-3-yl)ethanone (3ATI) Holmium(III), $[L]_t$ / $[M]_t$ graph in non-micellar medium at 298 K temperature.

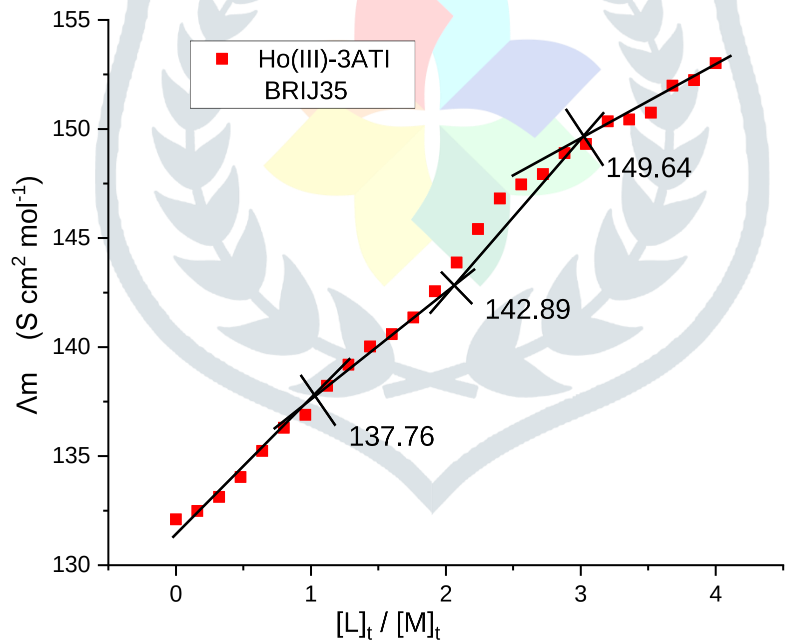

Figure-4. Molar conductance Λm (S cm2 mol-1) with 1-(1H-indole-3-yl)ethanone (3ATI) Holmium (III), $[L]_t$ / $[M]_t$ graph in micellar medium (BRIJ35) at 298 K temperature.

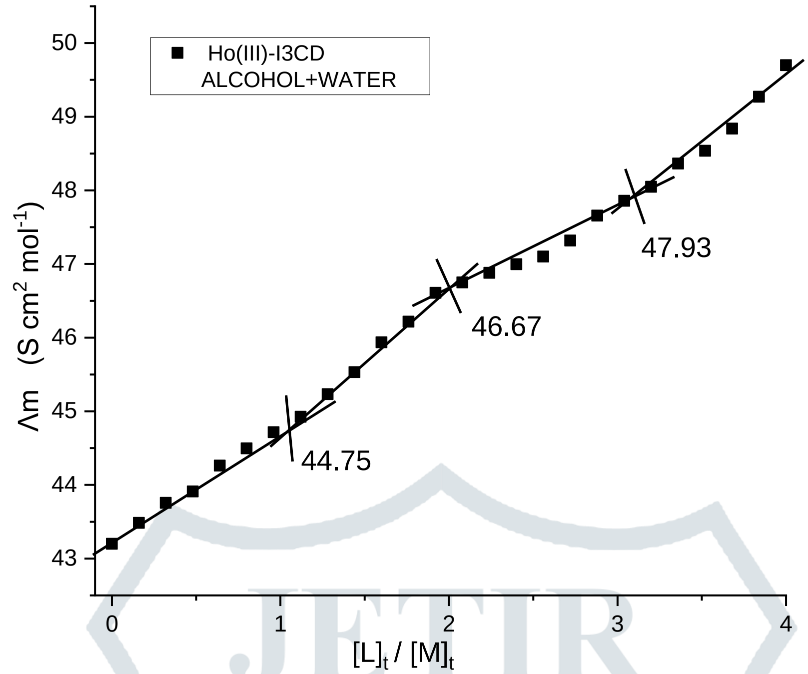

Figure-5. Molar conductance Λm (S cm2 mol-1) with 1H-indole-3-carbaldehyde (I3CD) Holmium(III), $[L]_t$ / $[M]_t$ graph in non-micellar medium at 298 K temperature.

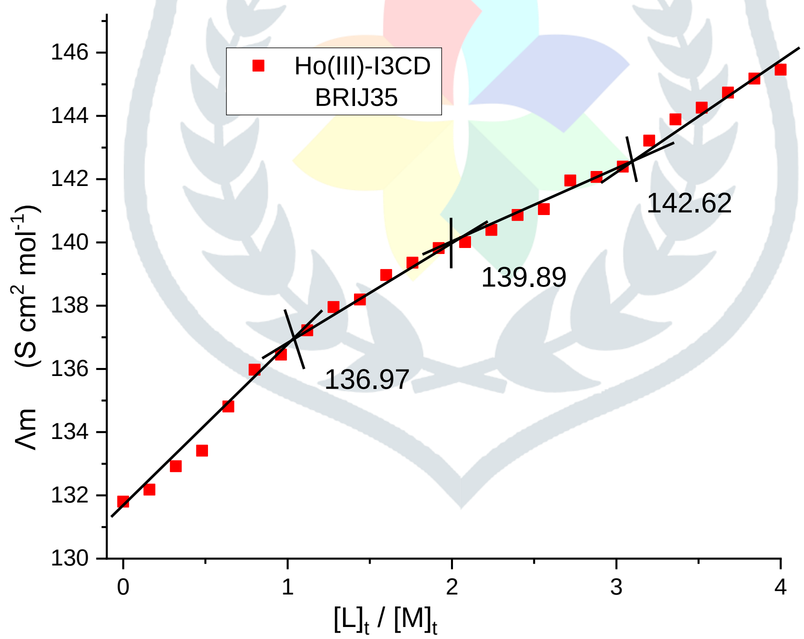

Figure-6. Molar conductance Λm (S cm2 mol-1) with 1H-indole-3-carbaldehyde (I3CD) Holmium (III), $[L]_t$ / $[M]_t$ graph in micellar medium (BRIJ35) at 298 K temperature.

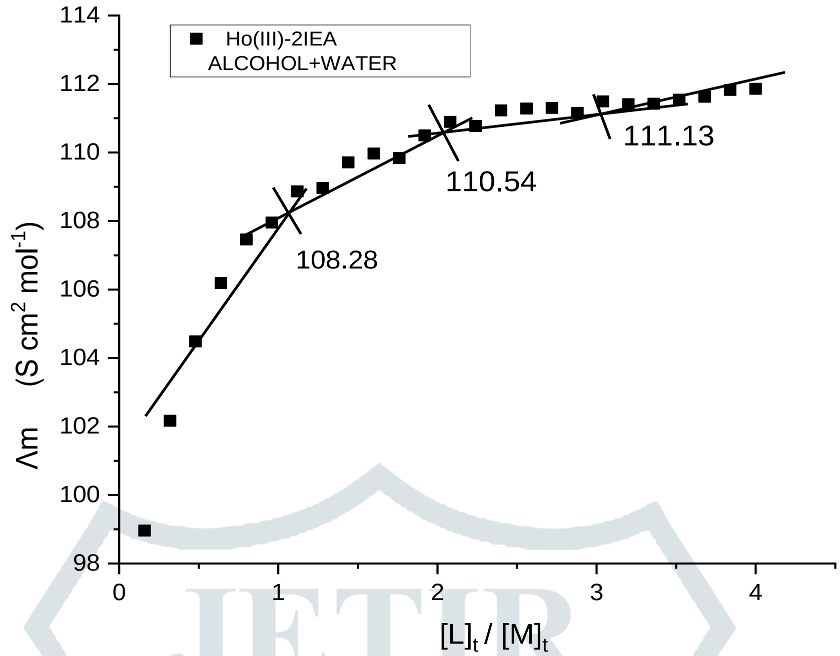

Figure-7. Molar conductance Λm (S cm2 mol-1) with 2-(1H-indole-3-yl)ethanoic acid (2IEA) Holmium(III), $[L]_t$ / $[M]_t$ graph in non-micellar medium at 298 K temperature.

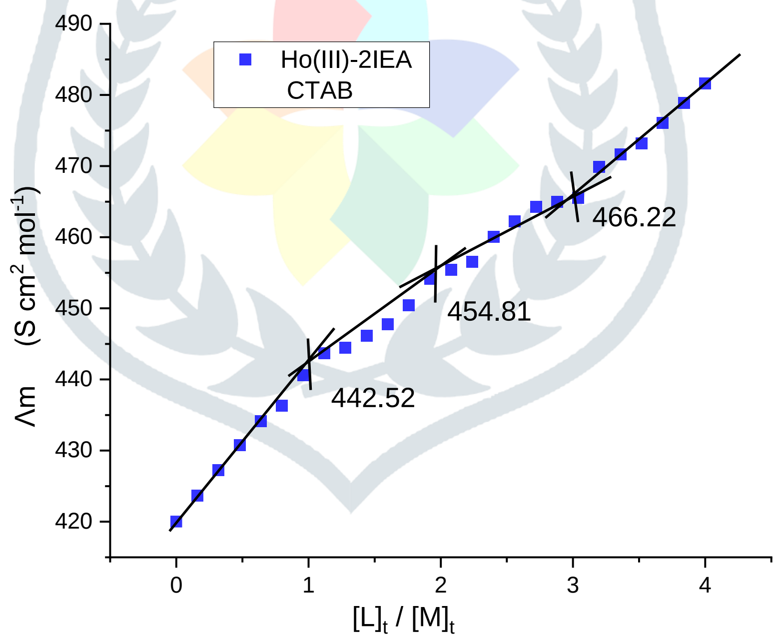

Figure-8. Molar conductance Λm (S cm2 mol-1) with 2-(1H-indole-3-yl)ethanoic acid (2IEA) Holmium(III), $[L]_t$ / $[M]_t$ graph in micellar medium (CTAB) at 298 K temperature.

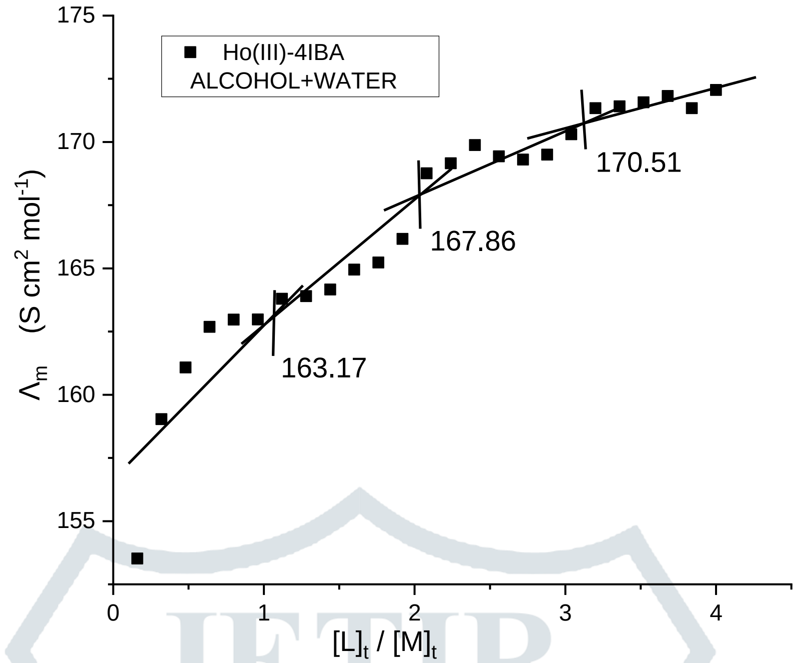

Figure-9. Molar conductance Λm (S cm2 mol-1) with 4-(1H-indole-3-yl)butanoic acid (4IBA) Holmium(III), $[L]_t$ / $[M]_t$ graph in non-micellar medium at 298 K temperature.

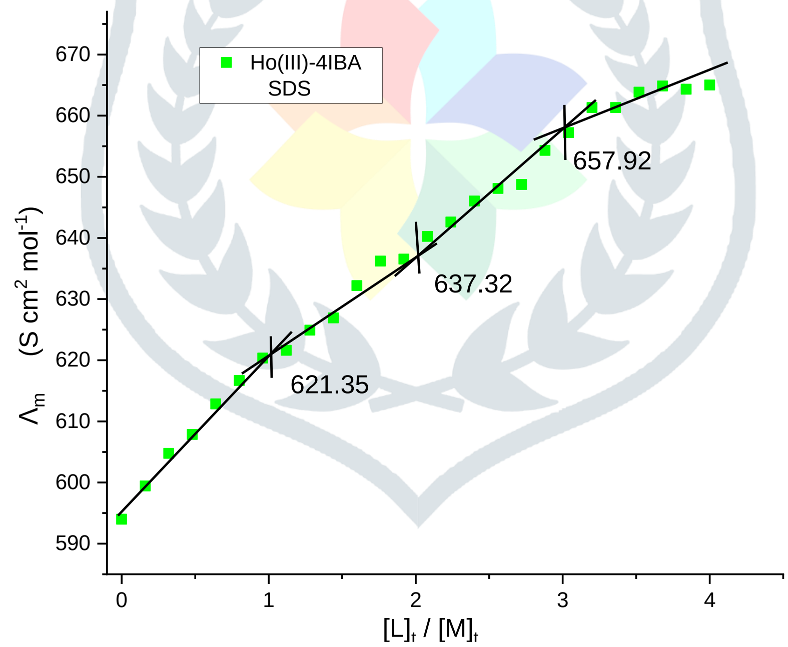

Figure-10. Molar conductance Λm (S cm2 mol-1) with 4-(1H-indole-3-yl)butanoic acid (4IBA) Holmium(III), $[L]_t$ / $[M]_t$ graph in micellar medium (SDS) at 298 K temperature.

Interaction between the Ho(III) ion with Indole derivative I3CA, 3ATI, I3CD, 2IEA, 4IBA are depicted as negative value of ΔG_A and spontaneously Association of metal-ligand complexes in different micellar medium BRIJ35, CTAB, SDS. Interaction between the metal ion Ho(III) and ligand I3CA, 3ATI, I3CD, 2IEA, 4IBA have been observed as complex formation between metal-ligand and decrease in conductance of solution. Due to the large size of metal-ligand Complex, mobility of the complex diminished as compared to free ion. In some cases, an enhancement in the conductivity have been observed. When metal salt is not fully dissociated then ligand combines with the Ho(III) metal ion but the metal salt anion remains undisturbed by ligand. Liberation of H^+ ion during the conductometric titration by

Indole derivatives, and migration of metal-ligand Complex towards the electrodes, increases conductivity of the solution [33].

To know about the metal-ligand interaction, stoichiometry of metal-ligand complexes and spontaneously complex formation, the conductometric titration between metal Ho(III) and ligand Indole derivatives has been done. The results of conductometric study, formation constant $\log K_f$ and Gibbs free energy of formation ΔG_f of Ho(III) with indole derivatives (I3CA, 3ATI, I3CD, 2IEA, 4IBA) with different metal-ligand ratio 1:1, 1:2, 1:3 [M:L] in different mediums BRIJ35, CTAB, SDS are represented in Table 3-4.

The value of thermodynamic parameters $\log K_f$ and ΔG_f of Ho(III)-I3CA are better in BRIJ35 micellar medium as compared to alcohol+water in 1:1, 1:2, 1:3 [M:L] ratio. Negative value of ΔG_f provide an idea about the Spontaneous formation of stable Complex Ho(III)-I3CA in micellar medium. On comparing all the five complexes 1:1, 1:2, 1:3 [M:L] ratio of Metal-ligand complexes in same medium 1:1 [M:L] ratio have higher value of ΔG_f, hence more spontaneously formation of metal-ligand stable complex Ho(III)-I3CA, Ho(III)-3ATI, Ho(III)-I3CD, Ho(III)-2IEA and Ho(III)-4IBA takes place.

The order of thermodynamic parameters $\log K_f$ and ΔG_f of Ho(III)-I3CA in different metal-ligand ratio are as follow [34-35]-

$\log K_f$ (1:1) BRIJ35> $\log K_f$ (1:1) Alcohol+Water > $\log K_f$ (1:2) BRIJ35> $\log K_f$ (1:2)Alcohol+Water > $\log K_f$ (1:3) BRIJ35> $\log K_f$ (1:3)Alcohol+Water

ΔG_f (1:1) BRIJ35> ΔG_f (1:1) Alcohol+Water > ΔG_f (1:2) BRIJ35 > ΔG_f (1:2)Alcohol+Water > ΔG_f (1:3) BRIJ35 > ΔG_f (1:3)Alcohol+Water

The order of $\log K_f$ and ΔG_f of Ho(III)-3ATI complex are as

$\log K_f$ (1:1) Alcohol+Water > $\log K_f$ (1:1) BRIJ35 > $\log K_f$ (1:2) Alcohol+Water > $\log K_f$ (1:2) BRIJ35 > $\log K_f$ (1:3) BRIJ35 > $\log K_f$ (1:3) Alcohol+Water.

ΔG_f (1:1) Alcohol+Water > ΔG_f (1:1) BRIJ35 > ΔG_f (1:2) Alcohol+Water > ΔG_f (1:2) BRIJ35 > ΔG_f (1:3) BRIJ35 > ΔG_f (1:3) Alcohol+Water.

The order of $\log K_f$ and ΔG_f of Ho(III)-I3CD complex are as

$\log K_f$ (1:1) BRIJ35 > $\log K_f$ (1:1) Alcohol+Water > $\log K_f$ (1:2)Alcohol+Water > $\log K_f$ (1:2) BRIJ35 > $\log K_f$ (1:3)Alcohol+Water > $\log K_f$ (1:3) BRIJ35

ΔG_f (1:1) BRIJ35 > ΔG_f (1:1) Alcohol+Water > ΔG_f (1:2)Alcohol+Water > ΔG_f (1:2) BRIJ35 > ΔG_f (1:3) Alcohol+Water > ΔG_f (1:3) BRIJ35

The thermodynamic parameters $\log K_f$ and ΔG_f of Ho(III)-2IEA are higher in micellar cationic surfactant for all 1:1, 1:2 while lower for 1:3 [M:L] ratio. Among these Ho(III)-2IEA, 1:1 [M : L] ratio have higher value of $\log K_f$ and ΔG_f as compared to 1:2 and 1:3 ratio in CTAB micellar medium.The order of $\log K_f$ and ΔG_f of Ho(III)-2IEA in different metal-ligand ratio are as follow-

$\log K_f$ (1:1) CTAB > $\log K_f$ (1:1) Alcohol+Water> $\log K_f$ (1:2) CTAB> $\log K_f$ (1:2) Alcohol+Water> $\log K_f$ (1:3)Alcohol+Water> $\log K_f$ (1:3) CTAB.

ΔG_f (1:1) CTAB> ΔG_f (1:1) Alcohol+Water > ΔG_f (1:2) CTAB> ΔG_f (1:2) Alcohol+Water > ΔG_f (1:3) Alcohol+Water> ΔG_f (1:3) CTAB.

Micellar medium SDS have higher value of $\log K_f$ and ΔG_f with some fluctuation towards lower concentration in same M:L ratio for complex Ho(III)-4IBA.
The order of $\log K_f$ and ΔG_f of Ho(III)-4IBA in different metal-ligand ratio are as [36-37]

$\log K_f$ (1:1) SDS>$\log K_f$ (1:1) Alcohol+Water >$\log K_f$ (1:2) SDS >$\log K_f$ (1:2) Alcohol+Water >$\log K_f$ (1:3) SDS > $\log K_f$ (1:3)Alcohol+Water.Some fluctuation occurs towards lower concentration

ΔG_f (1:1) SDS > ΔG_f (1:1) Alcohol+Water >ΔG_f (1:2) SDS > ΔG_f (1:2) Alcohol+Water >ΔG_f (1:3) SDS > ΔG_f (1:3)Alcohol+Water. Some fluctuation occurs towards lower concentration

The decreasing order of formation constant $\log K_f$ is observed as 1:1 > 1:2 > 1:3 [M:L] in non-micellar medium alcohol+water as well as in micellar medium. Ho(III) forms complexes with indole derivatives in 1:1, 1:2, 1:3 [M:L] in different stoichiometric ratio. Complexes of Ho(III) with indole derivative (I3CA, 3ATI, I3CD, 2IEA, 4IBA) in 1:1 metal-ligand stoichiometric ratio have higher value of $\log K_f$ and ΔG_f in non-micellar medium as well as in micellar medium as compare to 1:2 and 1:3 metal-ligand ratio. Ho(III)-I3CA, Ho(III)-3ATI, Ho(III)-I3CD, Ho(III)-2IEA and Ho(III)-4IBA complexes on 1:1, [M:L] stochiometric ratio are formed more stable complexes, spontaneously formation of complexes, feasible and more interaction with micellar medium as compared to 1:2 and 1:3 [M:L] ratio [38].

Stability constant $\log K_f$ decreases as the total concentration of ligand $C_{L[Ligand]}$ increases to obtained 1:1, 1:2, 1:3 [M:L] ratio. On higher concentration of $C_{L[Ligand]}$, $\log K_f$ decrease due to greater size of the ligand and overcrowding of the ligand. Micellar surfactant solvent, shows variation in $\log K_f$ 1:1, 1:2, 1:3 [M:L] ratio with variation in ligand and solvent system changes.

Table-1. Association Constant K_A and Gibbs Free Energy of Association ΔG_A for Ho(III) with Indole derivatives in non micellar [ALCOHOL+WATER] and micellar medium [BRIJ35] at 298 K.

$C_{m[Metal]}$	K_A of Ho(III)-I3CA		ΔG_A (kJ/mol) of Ho(III)-I3CA		K_A of Ho(III)-3ATI		ΔG_A (kJ/mol) of Ho(III)-3ATI		K_A of Ho(III)-I3CD		ΔG_A (kJ/mol) of Ho(III)-I3CD	
	ALCOHOL +WATER	BRIJ35	ALCOHOL+ WATER	BRIJ35	ALCOHOL +WATER	BRIJ35	ALCOHOL +WATER	BRIJ35	ALCOHOL+ WATER	BRIJ35	ALCOHOL+ WATER	BRIJ35
0.00098425	4802941.116	320299.8	-38.12366696	-31.413871	1649453.83	189000.325	-35.4751999	-30.106695	168402.9865	107251.3178	-29.82075914	-28.70271442
0.00096899	3944731.286	310541.7	-37.63587491	-31.337203	1482455.247	186940.957	-35.2106849	-30.079546	163944.9752	103405.8199	-29.75427643	-28.61223304
0.0009542	3412171.419	299460.2	-37.27648302	-31.24716	1469397.985	181339.669	-35.1887622	-30.0041624	163477.2729	101822.8938	-29.74719704	-28.57400644
0.00093985	2909745.902	295089	-36.88177654	-31.210722	1357479.805	172083.078	-34.9924464	-29.8743278	155797.7315	91301.76257	-29.62796618	-28.30374167
0.00092593	2515880.602	279698.3	-36.52136641	-31.077986	1239467.051	164315.82	-34.7670746	-29.7598754	152114.7682	82970.60865	-29.56868384	-28.0666358
0.00091241	2142588.053	244605.7	-36.1233758	-30.745773	1141310.783	161976.887	-34.562628	-29.7243489	148698.1958	80888.52332	-29.51239176	-28.00365824
0.00089928	1821728.964	234571.6	-35.72137074	-30.641977	1060131.786	150662.651	-34.3797894	-29.5449146	145553.8537	75941.9119	-29.45943013	-27.8472873
0.00088652	1601614.585	229279	-35.4022669	-30.585425	993715.7163	143467.368	-34.2194682	-29.4236512	138670.9946	71169.20294	-29.33939005	-27.68644272
0.00087413	1425205.163	213665.2	-35.11309093	-30.410653	940385.8432	137776.381	-34.0827785	-29.3233517	131969.022	70894.75713	-29.21663653	-27.6768684
0.00086207	1274325.457	103602.3	-34.83580365	-28.616937	878936.8389	134977.331	-33.9153208	-29.2724902	121430.8183	65433.39214	-29.01040962	-27.4782211
0.00085034	1077949.868	198070.4	-34.42109236	-30.222849	829517.1534	129713.215	-33.7719198	-29.1739124	115052.511	63493.0085	-28.8767055	-27.40362552
0.00083893	1002000.091	192092	-34.24004121	-30.146902	763549.785	119162.777	-33.5665776	-28.9636884	104826.5075	60679.82109	-28.64604667	-27.29132522
0.00082781	812789.3928	152732.5	-33.72143817	-29.578727	718018.9425	107431.793	-33.4142232	-28.7068807	102806.2228	60480.6334	-28.59782247	-27.28317749
0.00081699	702206.0871	148261.7	-33.35904013	-29.505107	602019.7105	93235.5749	-32.977582	-28.3556791	101086.1788	58216.19493	-28.55601216	-27.18861723
0.00080645	612457.0971	146897.1	-33.02017598	-29.482193	533201.3849	80587.6997	-32.6767729	-27.9944253	99680.15573	54970.12623	-28.52130308	-27.04644414
0.00079618	564326.4072	140018.5	-32.81735989	-29.363353	482085.4764	75913.7349	-32.4270438	-27.8463677	98603.46012	54500.97529	-28.49439114	-27.02520435
0.00078616	494585.9711	140715.6	-32.49047995	-29.375661	427181.006	72761.8744	-32.1274176	-27.7412861	93387.12295	46566.22594	-28.35970369	-26.63530529
0.0007764	425412.9765	129746.7	-32.11714024	-29.174552	375384.0134	64426.9172	-31.8071132	-27.4398088	83877.83385	46595.43338	-28.09358412	-26.63685907
0.00076687	373123.5535	127947.5	-31.79214614	-29.139948	331954.0785	61640.6945	-31.5024337	-27.3302575	78965.4557	44290.49563	-27.94403349	-26.51114317
0.00075758	323797.2196	120294.9	-31.44078258	-28.987119	295777.0346	52189.3506	-31.2164933	-26.9178067	74234.39487	36731.62003	-27.79093432	-26.04742627
0.0007485	260407.8723	100722	-30.90090088	-28.547067	261014.3152	52556.9338	-30.906665	-26.9351989	65098.07328	30659.22223	-27.46548964	-25.59963729
0.00073964	205485.2015	88869.93	-30.31391996	-28.236844	213671.8466	50444.3404	-30.4107297	-26.8335345	60669.76585	27511.11443	-27.29091455	-25.33116029
0.00073099	174434.8009	75719.54	-29.90796359	-27.840021	182242.6366	38436.1645	-30.0164709	-26.1598313	51771.85768	23150.6891	-26.89790388	-24.90353971
0.00072254	139206.3332	64181.5	-29.34893801	-27.430351	152027.306	36630.102	-29.5672586	-26.0405681	38408.56182	18962.58451	-26.15805104	-24.40903441
0.00071429	115884.2494	51362.4	-28.89455516	-26.878228	111393.0355	29172.1302	-28.7966064	-25.476431	25231.69784	16433.01716	-25.11683888	-24.05424351

Table-2. Association Constant K_A and Gibbs Free Energy of Association ΔG_A for Ho(III) with Indole derivatives in non-micellar [ALCOHOL+WATER] and micellar medium [CTAB, SDS] at 298 K.

$C_{m[Metal]}$	K_A of Ho(III)-2IEA		ΔG_A (kJ/mol) of Ho(III)-2IEA		K_A of Ho(III)-4IBA		ΔG_A (kJ/mol) of Ho(III)-4IBA	
	ALCOHOL +WATER	CTAB	ALCOHOL +WATER	CTAB	ALCOHOL +WATER	SDS	ALCOHOL +WATER	SDS
0.00098425	142804.9427	159475.7	-29.41218303	-29.685786	139327.6122	126458.9	-29.35109596	-29.110948
0.00096899	103346.2812	151717.5	-28.61080585	-29.562203	95998.6893	118329.9	-28.42805009	-28.946308
0.0009542	78379.98034	144152.4	-27.92559221	-29.435455	83002.33848	115019.9	-28.06758327	-28.876002
0.00093985	61641.17822	136774.3	-27.33027699	-29.305264	73397.35504	107229.1	-27.76283437	-28.702201
0.00092593	49880.69935	133251.5	-26.80569044	-29.240601	73462.4753	101958.7	-27.76503197	-28.57731
0.00091241	46153.17192	122557.5	-26.61322658	-29.033296	75630.54697	96873.96	-27.83710644	-28.450541
0.00089928	38032.3651	115709.3	-26.13366018	-28.890812	71408.07087	96875.78	-27.69474586	-28.450588
0.00088652	38090.07032	116539.7	-26.13741715	-28.908531	72677.59064	92227.97	-27.73841398	-28.328753
0.00087413	31352.98507	113932.9	-25.65508536	-28.852473	72599.04109	90330.05	-27.7357343	-28.277227
0.00086207	29518.38015	111606.5	-25.50566989	-28.801351	68188.80342	80946.52	-27.58043358	-28.005434
0.00085034	31734.44025	105535.6	-25.68505218	-28.662753	67801.44185	74264.22	-27.56631651	-27.79193
0.00083893	25400.95035	95621.96	-25.13340576	-28.418307	61867.60631	75599.62	-27.33936288	-27.836093
0.00082781	21771.84685	93902.29	-24.75137243	-28.373336	42692.88965	69251.52	-26.42010642	-27.618755
0.00081699	23711.9417	92493.53	-24.96289877	-28.335878	40702.39483	65767.37	-26.3017923	-27.490837
0.00080645	19183.42325	82944.14	-24.43772673	-28.065845	36066.91268	59726.49	-26.00217253	-27.252084
0.00079618	19068.66676	77719.19	-24.42285854	-27.904612	40593.87094	56627.57	-26.29517639	-27.120056
0.00078616	19342.1688	72665.24	-24.4581483	-27.737993	42729.66627	56649.14	-26.42224012	-27.121
0.0007764	21585.50981	72146.26	-24.73007272	-27.720231	42122.43483	45315.36	-26.38677238	-26.56783
0.00076687	17978.38748	71997.18	-24.27696232	-27.715105	36271.95849	39876.76	-26.01622054	-26.251009
0.00075758	19472.41941	58551.45	-24.4747794	-27.202847	28329.03696	31662.09	-25.40375938	-25.679396
0.0007485	19762.58377	54206.49	-24.51143268	-27.011779	28394.28644	32434.31	-25.40946037	-25.739108
0.00073964	18698.98648	50048.03	-24.37434593	-26.813989	27675.82705	27479.91	-25.34595227	-25.328348
0.00073099	17960.3126	41446.15	-24.27446975	-26.346665	26088.93834	25795.92	-25.19963035	-25.171641
0.00072254	15696.16601	32956.33	-23.94056175	-25.778674	31113.14115	27643.92	-25.63605615	-25.343093
0.00071429	15609.45804	24575.06	-23.92683486	-25.051496	25109.85283	26652.39	-25.10484343	-25.252579

Table-3. Formation Constant K_f and Gibbs Free Energy of Formation ΔG_f for metal ligand ratio 1:1 , 1:2 , 1:3 at 298 K for Ho(III) with indole derivatives in non-micellar [ALCOHOL+WATER] and micellar medium [BRIJ35, CTAB, SDS]

Complex M:L Ratio	$C_{L[Ligand]}$	log K_f of Ho(III)-I3CA		ΔG_f (kJ/mol) of Ho(III)-I3CA		log K_f of Ho(III)-3ATI		ΔG_f (kJ/mol) of Ho(III)-ATI		log K_f of Ho(III)-I3CD		ΔG_f (kJ/mol) of Ho(III)-I3CD	
		ALCOHOL +WATER	BRIJ35	ALCOHOL + WATER	BRIJ35	ALCOHOL +WATER	BRIJ35	ALCOHOL + WATER	BRIJ35	ALCOHOL + WATER	BRIJ35	ALCOHOL + WATER	BRIJ35
1:1	0.001007	4.4661213	4.399455	-25.4830108	-25.10262	4.982929183	4.58153541	-28.431838	-26.141546	4.50293645	4.59051902	-25.693072	-26.1928052
	0.001135	3.9912195	4.070276	-22.7732929	-23.22438	4.254143832	4.01258508	-24.273499	-22.895202	3.98537823	3.91123609	-22.739964	-22.3169199
	0.001259	3.7317735	3.730395	-21.2929337	-21.28507	3.964845421	3.74721601	-22.622807	-21.381046	3.70616705	3.75952549	-21.146827	-21.4512822
	0.001379	3.5407427	2.863133	-20.2029406	-16.3366	3.741070588	3.59486211	-21.345981	-20.511738	3.44844430	3.4677984	-19.6763	-19.7867316
	0.001497	3.3394441	3.417736	-19.0543615	-19.50108	3.581228716	3.43366721	-20.433948	-19.591984	3.29332334	3.33394049	-18.791203	-19.0229587
	0.001611	3.2347263	3.30572	-18.4568574	-18.86194	3.41991019	3.23844543	-19.513489	-18.478078	3.11771251	3.197529	-17.789195	-18.2446155
1:2	0.001722	3.9498201	3.906772	-22.5370742	-22.29145	4.197478226	3.85386416	-23.950174	-21.989564	4.44062828	4.54343756	-25.337551	-25.9241655
	0.00183	3.5432702	3.665517	-20.2173625	-20.91488	3.569854865	3.35912916	-20.36905	-19.166681	3.97935976	3.86008161	-22.705623	-22.0250402
	0.001935	3.3063245	3.542122	-18.8653861	-20.21081	3.332932318	3.08039637	-19.017206	-17.576274	3.74825938	3.5167629	-21.387	-20.0661156
	0.002038	3.174478	3.358528	-18.1130897	-19.16325	3.172663357	2.96107093	-18.102736	-16.895422	3.59257533	3.40570237	-20.49869	-19.4324211
	0.002138	3.018509	3.300406	-17.2231543	-18.83161	3.020103966	2.87169837	-17.232255	-16.385475	3.36479665	3.06293482	-19.199019	-17.4766415
	0.002236	2.8702069	3.117695	-16.3769651	-17.78909	2.881653523	2.72141688	-16.442278	-15.527992	3.11513322	3.01119841	-17.774478	-17.1814414
	0.002331	2.7503458	3.049433	-15.6930561	-17.3996	2.762156138	2.64795654	-15.760444	-15.108838	2.98505792	2.90196836	-17.032288	-16.5581913
1:3	0.002424	3.607234	3.825872	-20.5823302	-21.82985	3.536242707	3.51450836	-20.177264	-20.053252	3.93834372	3.42160393	-22.471592	-19.523153
	0.002515	3.1278268	3.196849	-17.8469052	-18.24074	3.220473653	3.44230784	-18.375534	-19.641286	3.29859756	2.99806471	-18.821297	-17.1065025
	0.002604	2.8352313	2.960898	-16.1773995	-16.89444	2.928317562	3.25689867	-16.708536	-18.58337	3.10093933	2.81742022	-17.693489	-16.0757724
	0.00269	2.6688885	2.748239	-15.228273	-15.68104	2.747881145	2.79949146	-15.678993	-15.973474	2.84084680	2.61158615	-16.209441	-14.9013144
	0.002775	2.4837564	2.572613	-14.1719373	-14.67894	2.579365677	2.71237446	-14.717469	-15.476397	2.52980309	2.42208163	-14.434673	-13.8200304
	0.002857	2.3446757	2.382512	-13.3783639	-13.59425	2.3521196	2.48349867	-13.420838	-14.170467	2.21517287	2.29486969	-12.63944	-13.0941783

Table-4. Formation Constant K_f and Gibbs Free Energy of Formation ΔG_f for metal ligand ratio 1:1 , 1:2 , 1:3 at 298 K for Ho(III) with indole derivatives in non-micellar [ALCOHOL+WATER] and micellar medium [CTAB, SDS]

Complex M:L Ratio	$C_{L[Ligand]}$	log K_f of Ho(III)-2IEA		ΔG_f (kJ/mol) of Ho(III)-2IEA		log Kf of Ho(III)-4IBA		ΔG_f (kJ/mol) of Ho(III)-4IBA	
		ALCOHOL + WATER	CTAB	ALCOHOL + WATER	CTAB	ALCOHOL + WATER	SDS	ALCOHOL + WATER	SDS
1:1	0.001007	3.84951526	4.58985	-21.96475	-26.18901	4.2454023	5.32643	-24.223622	-30.3918
	0.001135	3.7186173	4.3169	-21.217866	-24.63158	4.1249738	4.10772	-23.536475	-23.438
	0.001259	3.2660394	3.97525	-18.635525	-22.68217	3.9343279	3.85204	-22.448678	-21.9792
	0.001379	3.11897075	3.76093	-17.796374	-21.45932	3.6080383	3.47337	-20.586919	-19.8185
	0.001497	3.13622417	3.51935	-17.894819	-20.08087	3.4978627	3.26009	-19.958274	-18.6016
	0.001611	2.85033026	3.27495	-16.263552	-18.68635	3.2588733	3.21579	-18.594637	-18.3488
1:2	0.001722	3.5440298	4.51332	-20.221696	-25.7523	3.6006706	3.86056	-20.544881	-22.0277
	0.00183	3.72576935	4.01352	-21.258675	-22.90055	3.3853241	3.54778	-19.316146	-20.2431
	0.001935	3.13137679	3.46306	-17.867161	-19.75967	3.1102896	3.25941	-17.746841	-18.5977
	0.002038	3.06322075	3.25671	-17.478273	-18.58232	3.2328587	3.11487	-18.446202	-17.773
	0.002138	3.02715072	3.09428	-17.272463	-17.65549	3.2600806	3.06002	-18.601526	-17.46
	0.002236	3.13521239	3.03238	-17.889046	-17.30233	3.1694029	2.77085	-18.084132	-15.81
	0.002331	2.84072339	2.98091	-16.208737	-17.0086	2.9090035	2.62354	-16.598333	-14.9695
1:3	0.002424	3.247983	3.3377	-18.532498	-19.04442	3.2528119	3.27118	-18.560051	-18.6649
	0.002515	3.21191618	3.11924	-18.326707	-17.79791	3.1912597	3.25523	-18.208844	-18.5738
	0.002604	3.05005012	2.95116	-17.403123	-16.8389	3.0848204	2.92255	-17.601518	-16.6756
	0.00269	2.93945662	2.70339	-16.772094	-15.42515	2.9439514	2.80379	-16.79774	-15.998
	0.002775	2.735431	2.47924	-15.607954	-14.14618	3.1921256	2.8437	-18.213785	-16.2257
	0.002857	2.69317581	2.25143	-15.366853	-12.84631	2.8101024	2.76259	-16.034018	-15.7629

4. CONCLUSION

The main outcomes of Conductometric studies are interaction between metal Ho(III) ion and ligand indole derivatives in different greener solvent systems. In the presence of micellar surfactant medium more interaction are observed between the Holmium ion and indole derivatives. The Conductometric study, show the metal ligand interaction, in term of Association constant K_A and formation constant logK_f. By the replacement of non-micellar alcohol+water solvent by nonionic, cationic and anionic micellar solvents, enhancement in stability of metal-ligand complexes can be done.

Present study reveal the interaction in non-micellar solvent systems alcohol+water among Ho(III)-I3CA, Ho(III)-3ATI, Ho(III)-I3CD, Ho(III)-2IEA and Ho(III)-4IBA complexes and interaction of these complexes with nonionic, cationic and anionic surfactant micellar solvent systems. It is inferred that in micellar surfactant system more interaction of solvent system with Ho(III)-I3CA , Ho(III)-3ATI, Ho(III)-I3CD, Ho(III)-2IEA and Ho(III)-4IBA complexes have been observed and varies as the ligand system and surfactant medium changes. Extent of interaction of Ho(III) with indole derivatives shown by negative value of thermodynamic parameter ΔG_A. The result of $\log K_f$ and ΔG_f are finer in cationic, anionic and nonionic surfactant micellar systems CTAB, SDS, BRIJ35 respectively compared to non-micellar medium alcohol+water. The value of formation constant $\log K_f$ follow the order as $\log K_f$ (1:1) > $\log K_f$ (1:2) >$\log K_f$ (1:3) and the value of the Gibbs free energy of formation ΔG_f follow the order ΔG_f (1:1) > ΔG_f (1:2) > ΔG_f (1:3) for [M:L] ratio. This conclude that 1:1 metal ligand ratio show more interaction compare to 1:2 and 1:3 ratio. On moving towards higher concentration of ligand, stability of complexes decreases. High negative values of ΔG_f confirm the formation of stable and spontaneously formation of complex. Formation of more stable complexes between metal-ligand takes place when the metal ligand concentrations are in 1:1 ratio as compared to 1:2 and 1:3 ratio.

Micellar system increases the stabilization of the complexes by increasing the hydrophobic stabilization of H_2O molecule. By using micellar surfactant medium in conductometric titration stability of metal-ligand complexes of Ho(III) with I3CA , 3ATI, I3CD, 2IEA, 4IBA can be magnify which is observed that these complexes Ho(III)-I3CA, Ho(III)-3ATI, Ho(III)-I3CD, Ho(III)-2IEA and Ho(III)-4IBA have higher value of $\log K_f$ and ΔG_f in micellar surfactant medium as compared to non-micellar medium. For detection of metal-ligand complexes conductometric titration is highly sensitive as well as inexpensive technique. The use of eco-friendly micellar medium BRIJ35, CTAB, SDS in conductometric titration are greener chemicals which are non-toxic and safer for environment. Now a days, use of greener solvents for research purposes, are necessary requirement for sustainable development of ecosystem.

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