Spectroscopic and Thermodynamic Studies for the Complexation of Neodymium(III) with L(-) Asparagine(monohydrate) in Binary and Ternary Organic Solvent Mixtures

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Abstract- Neodymium(III) with L(-) asparagine(monohydrate) complexes in binary and ternary organic solvent mixtures had been spectrophotometrically and thermodynamically investigated. The observed spectra in the visible and near IR-region had been analyzed to calculate interelectronic repulsion parameter Slater-Condon (F_k), Lande spin-orbit coupling constant (ξ_{4f}), covalency parameters (β , $b^{1/2}$ and δ) and intensity parameters such as oscillator strengths (P) and Judd-Ofelt parameters (T_{λ}). The degree of covalency in the complexes increases with increase in oscillator strength values. The hypersensitive band (${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$) was correlated with the one of the most intense band of pseudo-hypersensitive i.e., ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ transition band to determine the degree of sensitivity of ligand and solvent environment on the complexation. The higher values of covalency parameters and oscillator strength are taken as evidence of participation of f-orbitals in bonding. The positive values of standard enthalpy (ΔH °) and standard entropy (ΔS °) confirmed the endothermic nature and the increasing randomness respectively. The negative values of standard free energy (ΔG °) favours the formation of neodymium (III) with L(-) asparagine(monohydrate) complex in the solution.

Keywords- Neodymium(III); L(-) Asparagine(monohydrate); Hypersensitive; Pseudo-hypersensitive

I. INTRODUCTION

Amino acids can be regarded as the building blocks of peptides and proteins and therefore are of fundamental significance to all organisms. Its compounds are also generally biologically active, generating significant interest in their metal complexes. Among the 20 most common natural amino acids in living organism asparagine is one of them and is also one of the eleven nonessential amino acids which the body can create for itself. Asparagine has carboxamide as the side chain functional group [1]. It plays a vital role in metabolic control of some cell functions in nerve and brain tissues and can also be used as nitrogen reserve source by plants [2]. The L form of amino acids are used in human protein structures and are more compatible to human biochemistry than the D-form [3] and hence L-form of asparagine(monohydrate) is considered as a ligand for the present study. Besides, lanthanides are known to form complexes with various functional groups found in biological molecules, especially with donor atom oxygen which is more favourable than nitrogen and sulphur donor atoms. Lanthanides which can bind the active sites of biomolecules replacing various ions that include Ca(II), Zn(II), Mg(II), Mn(II), Fe(II) and Fe(III). Consequently, the unique spectroscopic and magnetic properties of lanthanides made them an extensively used as structural and functional probes in understanding structures, conformation and characteristics of biomolecules [4]. For these reasons, many researchers are utmost interested in the connection between structure and function of metal complexes in biological system. So, a prodigious amount of work on absorption spectral study of trivalent lanthanide complexes in solution has been published in the last several years by many researchers [5-14].

In this paper we made an attempt to study the interaction between Nd(III) ion with L (-) asparagine(monohydrate) in binary and ternary solvent mixtures by absorption spectral analysis. The nature of coordination in these complexes was examined by analysing its energy interaction parameters like Slater-Condon (F_k), Lande spin-orbit coupling constant (ξ_{4f}), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), percent covalency parameter (δ) and intensity parameters like oscillator strengths ($P \times 10^6$) and Judd-Ofelt intensity parameters T_{λ} ($\lambda=2, 4, 6$). We had also determined the calculated oscillator strengths and compared with the experimental values. Again, the thermodynamic parameters like the standard enthalpy change (ΔH [°]), entropy change (ΔS [°]) and free energy change (ΔG [°]) for the complexation of Nd(III) with L (-) asparagine (monohydrate) complexes in H₂O:DMF (equimolar) had also been evaluated for interpretation of thermodynamics results to gain insight into the molecular interactions that regulate the process.

II. EXPERIMENTAL DETAILS

A. Materials and methods

Neodymium(III) nitrate hexahydrate of 99% purity was obtained from Central Drug House (P) Ltd., India and L (-) asparagine(monohydrate) of 99% purity from Loba, India had been used for spectral analysis. The solvents used in the study were CH_3OH , DMF, CH_3CN and $C_4H_8O_2$ which were of AR grade from E. Merck.

A Perkin Elmer Lambda-35 UV-Visible spectrophotometer and a quartz cell of 1.0 cm path length were used to record the absorption spectra in the range of 350-920 nm with Peltier-temperature control system. The pH meter adjustments were performed using a Systemics μ pH system (model 362) equipped with a combined glass electrode.

The sample solutions of Nd(III) and Nd(III):L(-)Asn (where L(-)Asn is a L(-) asparagine(monohydrate)) were prepared in concentration of 1×10^{-2} M in different solvents (50%, v/v). The pH was maintained at pH 5.4 [15, 16]. The absorption titrations were done for the determination of the equilibrium constants at various temperatures (298, 303, 308 and 313 K) by mixing various concentrations of L(-) Asn solution (6.7×10^{-4} M - 1×10^{-2} M) with constant concentrations and volumes of the Nd(III) solution in H₂O:DMF (equimolar).

B. Theoretical

1) Energy of 4f-4f transitions:

The energy of 4f-4f transitions are comprised of two main constituents and are given by Coulombic (represented by Slater-Condon, F_k) and spin-orbit interaction (represented by Lande, ξ_{4f} between 4f electrons), while f^k and A_{so} are the angular components of spin-orbit coulombic interaction as given as

$$\mathbf{E} = \mathbf{f}^{k} \mathbf{F}_{k} + \mathbf{A}_{so} \boldsymbol{\xi}_{4f} \tag{1}$$

By using the observed band energies (E_{obs}) and the zero order energies (E_{oj}) and partial derivatives of Nd (III) ion given by Wong [17] the correction factors are then added to the zero order parameters to obtain the spin-orbit interaction parameter (ξ_{4f}). The Slater integrals F_k have been evaluated from Racah parameters using relevant expressions. We outlined a calculational procedure for estimation of the values of inter-electronic repulsion parameters i.e., Slater-Condon (F_k) and Lande spin-orbit interaction parameter (ξ_{4f}), in our recent publications [18, 19]. The root mean square deviations (r.m.s) between the observed energies (E_{obs} .) and calculated energies ($E_{cal.}$) have been evaluated.

Nephelauxetic ratio:

The nephelauxetic ratio (β) is defined as the ratio of the inter electron repulsion parameters in the complex and in the free ion, [20, 21] i.e.,

$$\beta = \frac{F_k^c}{F_k^f} \quad \text{or} \quad \frac{E_c^k}{E_f^k} \tag{2}$$

where F_k (k = 2,4,6) is the Slater-Condon parameter and E_c^k and E_f^k are the Racah energy parameters for complex and free ions, respectively.

Bonding parameter:

The amount of mixing of '4f' orbitals and ligand orbitals represented by $b^{1/2}$ (bonding parameter) is related to nephelauxetic effect (1- β) by the following relation [22],

$$b^{\frac{1}{2}} = \left[\frac{1-\beta}{2}\right]^{\frac{1}{2}}$$
(3)

In addition to measuring the nephelauxetic ratio (β), the covalency parameter (δ) will be deduced.

Covalency parameter:

The covalency parameter [23] is defined as

$$\delta = \left[\frac{1-\beta}{\beta}\right] \times 100 \tag{4}$$

2) Spectral Intensities of 4f-4f Transitions:

The intensity of an absorption band is evaluated by its oscillator strength and which is directly proportional to the area under the absorption curve. The experimental value of oscillator strength (P_{obs}) of absorption band is evaluated by using Gaussian curve analysis [24] as:

$$\mathbf{P}_{\text{obs.}} = 4.6 \times 10^{-9} \times \varepsilon_{\text{max}} \times \Delta \bar{\mathbf{v}}_{\frac{1}{2}}$$
(5)

where, $\Delta \bar{v}_{y_{v}} =$ half-band width and $\varepsilon_{max} =$ molar extinction coefficient corresponding to energy \bar{v} in wave number.

Again, the calculated oscillator strength (P_{cal}) is evaluated using the Judd-Ofelt [25-26] theory of the transition of the induced-dipole transition $\Psi_{I} \rightarrow \Psi'_{J}$ of energy $\overline{\nu}$ (cm¹) can be expressed as:

$$\mathbf{P}_{\text{cal.}} = \sum_{\lambda=2,4,6} T_{\lambda} \overline{\mathbf{v}} \left| \left\langle \mathbf{f}^{N} \Psi_{J} \right\| \mathbf{U}^{(\lambda)} \left\| \mathbf{f}^{N} \Psi_{J}^{'} \right\rangle \right|^{2}$$
(6)

where, $T_{\lambda}(\lambda = 2,4,6)$ are the Judd-Ofelt intensity parameters. These three phenomenological parameters are related to the radial part of 4f^N wave function, wave function of perturbing configuration and ligand field parameters that characterized them and the immediate environment around the metal ion. $\overline{\nu}$ is the energy of transition while the values of reduced matrix elements $U^{(\lambda)}$ have been taken from Carnall *et al.* [27].

Relation (6) can be reduced to

$$\frac{\mathbf{P}_{\text{cal.}}}{\overline{\mathbf{v}}} = \left[\mathbf{U}^{(2)}\right]^2 \cdot \mathbf{T}_2 + \left[\mathbf{U}^{(4)}\right]^2 \cdot \mathbf{T}_4 + \left[\mathbf{U}^{(6)}\right]^2 \cdot \mathbf{T}_6 \tag{7}$$

The values of T_{λ} parameters have been computed from the Judd-Ofelt expression by using the partial and multiple regression method.

3) Thermodynamics parameters:

Thermodynamics classifies the energetic behavior of chemical systems at equilibrium in terms of macroscopic concepts such as temperature, pressure, enthalpy, entropy, free energy, etc. The temperature dependence of an equilibrium constants are considered with the purpose of more portray the interaction between Nd(III) and L(-) Asn. The equilibrium constant of the Nd(III):L(-) Asn complex in H₂O:DMF (equimolar) is calculated by applying the Benesi-Hildebrand equation from the Benesi-Hildebrand plot [28]

$$\frac{\left[A_{\circ}\right]}{\Delta A} = \frac{1}{\left[L(-)Asn\right]\epsilon.K} + \frac{1}{\epsilon}$$
(8)

where $[A_o]$ is the initial concentration of Nd(III), [L(-)Asn] is the concentration of the ligand, ΔA is the absorbance change due to the addition of L(-)Asn to Nd(III), and ε represents the molar extinction coefficient of complex. The plot of $[A_o]/\Delta A$ vs 1/[L(-)Asn] gives a straight line. The value of equilibrium constant (K) is calculated from the y-intercept value, which is equal to $1/\varepsilon$, and the slope value, which is equal to $1/\varepsilon$. These equilibrium constants can be used to evaluate the thermodynamic parameters.

Moreover, in the analysis of the temperature dependence of equilibrium constants are generally analysed by using the empirical the van't Hoff equation. According to van't Hoff equation,

$$\ln K = \frac{-\Delta H^{\circ}}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^{\circ}}{R}$$
(9)

where ΔH° and ΔS° are change in the standard enthalpy and entropy of reaction respectively. The values of ΔH° and ΔS° are evaluated from the slope and intercept of the van't Hoff plots [29].

The change in standard free energy [30-32] of complexation is calculated by using the following equation,

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{10}$$

III. RESULTS AND DISCUSSIONS

A. Spectral Energy and Intensity of 4f-4f Transition Study

The absorption spectra of 4f-4f transition bands of Nd(III) with L(-) As complexes in different binary and its ternary solvent mixtures are recorded in the visible and near infrared region appear due to transitions from the ground levels of ${}^{4}I_{9/2}$, to the excited J-levels of the 4f³ configuration. Figs. 1-3 show the comparative absorption spectra of Nd(III) and Nd(III):L(-) As n in binary and ternary solvent mixtures respectively. From these figures, we can observe only five bands in the 400-920 nm spectral regions which are designated as ${}^{4}I_{9/2} \rightarrow {}^{4}G_{7/2}$, ${}^{4}G_{5/2}$, ${}^{4}F_{5/2}$ and ${}^{4}F_{3/2}$ transitions respectively and depicts as a slightly red shifts. The band due to ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$ transition band has been found to obey the selection rules of $|\Delta J|$, $|\Delta L| \le 2$ and $|\Delta S| = 0$ and depends on $|U|^2$ matrix elements and is a hypersensitive band and the remaining bands are considered as a pseudo hypersensitive bands [33-35].



Fig. 1 Comparative absorption spectra of Nd (III) free ion and Nd(III):L(-) Asn complex in H₂O:DMF (equimolar).



Fig. 2 Comparative absorption spectra of Nd (III):L(-) Asn complexes in binary solvent mixtures (equimolar). In the inset, the enlargement of ${}^4I_{9/2} \rightarrow {}^4F_{5/2}$ transition is shown.



Fig. 3 Comparative absorption spectra of Nd (III):L(-) Asn complexes in ternary solvent mixtures (equimolar). In the inset, the enlargement of ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ transition is shown.

Upon examining spectra of Fig.1, Nd(III):L(-)Asn is found to be more intensified than the Nd(III) free ion. Fig. 2 shows that the intensification of bands (except ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ transition band) of Nd(III):L(-)Asn in H₂O:DMF is more than H₂O:CH₃OH, H₂O:C₄H₈O₂ and H₂O:CH₃CN. On the other hand, H₂O:DMF:C₄H₈O₂ shows greater intensification of the bands than H₂O:CH₃CN:DMF, H₂O:CH₃OH:DMF, H₂O:CH₃OH:C₄H₈O₂, H₂O:CH₃CN:CH₃OH and H₂O:CH₃CN:C₄H₈O₂ respectively and are depicted in Fig.3. Thus, Figs. 2-3 show the solvent effects on complexation. As can be seen from Figs. 1-3, that the ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ transition band induces more than the ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$ transition band, which may show the sensitivity towards even minor changes in the immediate coordination environment around Nd(III) [13]. The change in the structure of the band is due to different symmetries i.e., different geometrical arrangement of the environment around the Nd(III) ion in the H₂O:DMF solvent [36]. The shape and intensity of spectral bands are used in complexation studies of Nd(III) with L(-) Asn in different solvents. The complexation of Nd(III) can be depicted by evaluating its energy and intensities parameters. The energy parameters such as Slater-Condon (F_k), Lande spin-orbit coupling constant (ξ_{4f}), nephelauxetic ratio (β), bonding parameter (b^{1/2}) and percent covalency (δ) are evaluated and presented in Table I.

TABLE I COMPUTED VALUES OF ENERGY INTERACTION LIKE SLATER-CONDON, F_k (CM⁻¹); LANDE SPIN-ORBIT COUPLING, Ξ_{4F} (CM⁻¹); NEPHELAUXETIC RATIO, B; BONDING PARAMETER, $B^{\frac{1}{2}}$ AND PERCENT COVALENCY PARAMETERS, Δ OF ND(III) AND ND(III):L (-) ASN (1:1) IN THE SOME SELECTED BINARY (EQUIMOLAR) AND TERNARY ORGANIC SOLVENT MIXTURES (EQUIMOLAR).

System	\mathbf{F}_2	\mathbf{F}_4	\mathbf{F}_{6}	ξ _{4f}	β	b ^{1/2}	δ
1. H ₂ O:CH ₃ OH							
Nd(IIII)	332.0457	48.6702	5.1089	898.3106	0.0604	0.9927	0.7341
Nd(IIII): L(-)Asn	331.9827	48.6507	5.1099	899.3814	0.0581	0.9932	0.6808
2. H ₂ O:CH ₃ CN							
Nd(IIII)	332.0851	48.6129	5.0997	897.3977	0.0643	0.9917	0.8331
Nd(IIII): L(-)Asn	332.0381	48.6063	5.1025	898.4266	0.0618	0.9924	0.7708
3. H ₂ O:C ₄ H ₈ O ₂							
Nd(IIII)	331.8640	48.6057	5.1168	902.4482	0.0503	0.9949	0.5083
Nd(IIII): L(-)Asn	331.8285	48.6040	5.1190	903.1665	0.0480	0.9954	0.4636

148.42

149.87

60.88

60.57

(11438.44)

11540.68

(11437.17)

11558.02

(11555.23)

11557.35

(11553.06)

(12551.73)

12501.25

(12550.88)

12591.92

(12628.03)

12591.45

(12627.31)

Nd(IIII)

Nd(IIII) : L(-)Asn

5.H2O:CH3CN:CH3OH

Nd(IIII)

Nd(IIII) : L(-)Asn

(19209.59)

19144.25

(19209.94)

19177.66

(19176.02)

19174.72

(19175.40)

4. H ₂ O: DMF									
Nd(IIII)	329.3694	49.9595	5.2808	927.7618	0.0937	1.0175	1.7240		
Nd(IIII):L (-)Asn	329.3378	49.9742	5.2826	928.0727	0.0944	1.0178	1.7494		
5. H ₂ O:CH ₃ CN:CH ₃ O	5. H ₂ O:CH ₃ CN:CH ₃ OH								
Nd(IIII)	332.0962	48.6699	5.1069	897.5461	0.0622	0.9923	0.7808		
Nd(IIII):L (-)Asn	332.0503	48.6525	5.1084	898.5084	0.0602	0.9927	0.7305		
6. H ₂ O:CH ₃ CN:C ₄ H ₈ O	O_2								
Nd(IIII)	332.0012	48.6427	5.1115	899.6457	0.0574	0.9934	0.6626		
Nd(IIII):L(-)Asn	331.9382	48.6352	5.1129	900.5620	0.0552	0.9939	0.6127		
7. H ₂ O:CH ₃ CN:DMF									
Nd(IIII)	331.5919	48.6364	5.1709	913.8550	0.0384	1.0029	0.2940		
Nd(IIII):L (-)Asn	331.5306	48.6683	5.1741	914.3496	0.0412	1.0034	0.3390		
8. H ₂ O:CH ₃ OH:C ₄ H ₈	O_2								
Nd(IIII)	331.8929	48.6195	5.1135	901.3471	0.0534	0.9943	0.5744		
Nd(IIII) : L(-)Asn	331.8386	48.6314	5.1174	902.2746	0.0503	0.9949	0.5088		
9. H ₂ O:CH ₃ OH:DMF									
Nd(IIII)	331.5523	48.6327	5.1690	913.9007	0.0379	1.0029	0.2870		
Nd(IIII) :L (-)Asn	331.5142	48.6408	5.1708	914.3941	0.0401	1.0032	0.3207		
10. H ₂ O:DMF:C ₄ H ₈ O ₂									
Nd(IIII)	331.4341	48.6294	5.1778	916.5294	0.0477	1.0045	0.4522		
Nd(IIII):L (-)Asn	331.4021	48.6339	5.1791	916.9488	0.0491	1.0048	0.4793		

Where L(-) Asn is denoted as L (-) asparagine (monohydrate).

From Table I, we can see that the values of Slater-Condon parameters, F_2 seem to decrease for all the systems and the values of F_4 are also decreased (except some systems). Unfortunately, F_6 and ξ_{4f} parameters exhibit a slight increase in the complexes from the corresponding Nd(III) free ion. The values of nephalauxetic ratio (β) are less than unity. The bonding ($b^{1/2}$) and covalency (δ) parameters has been found to be positives in all the systems. Moreover, the positive values of covalency (δ) in all the systems indicate electron delocalization over 4f orbitals. The analysis of Table I reveals that the mode of bonding might be covalent bonding in the complexes.

The comparison of the observed and calculated values of the energies of Nd(III) and Nd(III):L(-) As along with root mean square (r.m.s) deviation in its binary and ternary solvent mixtures are presented in Table II.

System	$\frac{{}^{4}I_{9/2} \rightarrow {}^{4}G_{7/2}}{E_{obs}}$ (E_{cal})	$\frac{{}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}}{E_{obs}}$ (E_{cal})	$\frac{{}^{4}I_{9/2} \rightarrow {}^{4}F_{7/2}}{E_{obs}}$ (E_{cal})	$\frac{{}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}}{E_{obs}}$ (E_{cal})	$\frac{{}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}}{E_{obs}}$ (E_{cal})	r.m.s.
1. H ₂ O:CH ₃ OH						
Nd(IIII)	19175.46 (19175.89)	17390.40 (17410.19)	13510.59 (13466.55)	12590.65 (12627.04)	11558.56 (11553.11)	60.71
Nd(IIII) : L(-)Asn	19171.41 (19175.06)	17387.07 (17405.87)	13510.23 (13466.39)	12589.70 (12626.18)	11558.42 (11550.61)	60.66
2. H ₂ O:CH ₃ CN						
Nd(IIII)	19172.51 (19173.65)	17395.54 (17416.67)	13513.15 (13468.14)	12594.46 (12629.59)	11561.36 (11556.71)	61.07
Nd(IIII) : L(-)Asn	19170.31 (19173.47)	17390.40 (17412.16)	13512.60 (13467.84)	12593.35 (12628.54)	11561.23 (11554.16)	61.45
3. H ₂ O:C ₄ H ₈ O ₂						
Nd(IIII)	19164.43 (19173.84)	17374.99 (17393.55)	13510.59 (13466.13)	12587.48 (12623.78)	11555.35 (11543.67)	62.16
Nd(IIII) : L(-)Asn	19162.96 (19173.79)	17371.67 (17390.27)	13510.04 (13465.83)	12586.53 (12622.95)	11555.08 (11541.80)	62.62
4. H ₂ O: DMF		•	•	•	•	•
	19144.62	17271.16	13382.58	12501.41	11541.08	1.40.40

TABLE II OBSERVED AND CALCULATED VALUES OF ENERGIES (CM^{-1}) and root mean square (r.m.s.) deviation values of nd(III) and nd(III):L(-) asn (1:1) in the some selected binary (equimolar) and ternary organic solvent mixtures (equimolar).

(13417.57)

13380.43

(13417.00)

13511.69

(13466.99)

13511.51

(13466.91)

(17211.87)

17269.96

(17209.69)

17394.03

(17413.87)

17390.70

(17410.06)

6.H ₂ O: CH ₃ CN:C ₄ H ₈ O ₂						
Nd(IIII)	19172.51	17388.58	13510.96	12590.81	11554.15	50.28
	(19175.12)	(17405.14)	(13466.61)	(12626.19)	(11550.28)	39.20
	19169.21	17385.86	13509.86	12589.70	11554.02	50 00
Nu(IIII) : L(-)ASII	(19174.63)	(17401.01)	(13466.22)	(12625.18)	(11547.87)	38.82
7. H ₂ O:CH ₃ CN:DMF						
Nd(IIII)	19162.96	17291.76	13503.11	12580.04	11550.41	<u>81 20</u>
Nu(IIII)	(19179.07)	(17341.62)	(13462.22)	(12610.75)	(11515.06)	81.50
Nd(IIII) J. () Asp	19162.23	17290.27	13500.01	12577.98	11550.28	80.25
Nu(IIII) :L (-)ASII	(19179.81)	(17337.75)	(13461.07)	(12609.14)	(11512.79)	80.55
8.H ₂ O:CH ₃ OH:C ₄ H ₈ O ₂						
NJ(IIII)	19166.27	17384.35	13509.50	12589.38	11553.08	58.40
Nd(IIII)	(19173.96)	(17397.88)	(13466.13)	(12624.58)	(11546.06)	
Nd(IIII) + I () A an	19164.80	17380.42	13508.95	12586.22	11552.81	50.09
Nu(IIII) : L(-)ASII	(19174.34)	(17393.03)	(13465.41)	(12623.12)	(11543.30)	39.98
9. H ₂ O:CH ₃ OH:DMF						
N.I/IIII)	19160.39	17295.95	13502.75	12578.93	11549.88	70.20
Nd(IIII)	(19178.44)	(17341.22)	(13462.02)	(12610.59)	(11514.72)	79.20
Nd(IIII) d. () Ase	19159.29	17294.16	13501.29	12578.14	11549.61	70.02
Nu(IIII) :L (-)ASII	(19178.58)	(17338.48)	(13461.52)	(12609.70)	(11513.14)	79.02
10. H ₂ O:DMF:C ₄ H ₈ O ₂						
NJ(IIII)	19155.99	17283.69	13500.92	12575.61	11548.01	02 47
Nd(IIII)	(19178.53)	(17329.16)	(13460.94)	(12607.54)	(11507.91)	02.47
Nd(IIII) : I ()Acr	19154.89	17282.20	13499.83	12574.98	11547.88	82 50
Nd(1111) : L(-)Asn	(19178.57)	(17326.93)	(13460.58)	(12606.86)	(11506.62)	02.39

In Table II, the decreasing order of energy for binary solvent mixtures are $H_2O:DMF < H_2O:C_4H_8O_2 < H_2O:CH_3OH < H_2O:CH_3CN$ and for ternary solvent mixtures are $H_2O:DMF:C_4H_8O_2 < H_2O:DMF:CH_3CN < H_2O:CH_3OH:DMF < H_2O:CH_3OH:C_4H_8O_2 < H_2O:CH_3CN:C_4H_8O_2 < H_2O:CH_3CN:C_4H_8$

An investigation based on the AO model inspects the relationship between the nephelauxetic effect, and geometric and energy parameters. The parameter η is defined as

$$\eta = \left(1 - \beta^{\frac{1}{2}}\right) / \beta^{\frac{1}{2}} \tag{11}$$

and η is proportional to nephelauxetic effect. From the first approximation, the parameter η may be inscribed as

$$\eta \approx \frac{H_{\rm L}^2}{\left(H_{\rm M} - H_{\rm L}\right)^2} \left(S_{\rm R}^*\right)^2 N,\tag{12}$$

where N is the coordination number. The equation for complexes with ligands containing identical donor atoms may be written as

$$\eta \approx \text{constant} \left(\mathbf{S}_{R}^{*}\right)^{2} \mathbf{N},$$
 (13)

where the constant is equal to $\frac{H_L^2}{(H_M - H_L)^2}$

Equation (13) has two variables, S_R^* and N which vary with changes in the lanthanide-ligand distance in opposing directions. Any variation in R leads to more changes in $(S_R^*)^2$ than in N. Therefore, the nephelauxetic effect increases when the coordination number decreases i.e., decrease in lanthanide-ligand distance in spite of the additive nature of β and decrease in the number of coordinated ligands [13].

The values of oscillator strengths (P) and Judd-Ofelt intensity parameters (T_{λ}) for all the systems are presented in Table III.

	$^{4}I_{9/2} \rightarrow ^{4}G_{7/2}$	$^{4}I_{9/2} \rightarrow ^{4}G_{7/2}$	$^{4}I_{9/2} \rightarrow ^{4}F_{7/2}$	$^{4}I_{9/2} \rightarrow ^{4}F_{5/2}$	$^{4}I_{9/2} \rightarrow ^{4}F_{3/2}$			
System	Pobs	Pobs	P_{obs}	Pobs	Pobs	т.	т.	Т
System	(P_{cal})	(P_{cal})	(P_{cal})	(P_{cal})	(P_{cal})	12	14	16
1 HOCHOH								
1. 1120.0113011	0 7589	2 6367	2 8441	5 5772	0 3848	1		
Nd(IIII)	(1.5857)	(2.5909)	(4.0134)	(4.2182)	(1.1969)	0.69	29.09	67.04
Nd(IIII) · L (-)Asn	0.9163	3.2038	3.2733	5.6205	0.4742	4 87	27 55	72 16
	(1.6367)	(3.1638)	(4.2991)	(4.4285)	(1.1882)	4.07	27.55	72.10
2. H ₂ O:CH ₃ CN						r		
Nd(IIII)	0.4759	1.4775	1.7296	2.2271	0.2189	4.68	7.43	33.97
	(0.6294)	(1.4690)	(1.9936)	(1.9216)	(0.4124)			
Nd(IIII) : L(-)Asn	(0.8144)	(2.3267)	(2.8740)	(2.6609)	(0.4802)	10.10	6.31	49.41
3. H ₂ O:C ₄ H ₈ O ₂	• • •	•	• • •	• • •		•		
Nd(IIII)	0.6499	2.7407	2.7742	2.9344	0.4106	12.42	6 77	50.50
Nu(IIII)	(0.8651)	(2.7288)	(2.9445)	(2.7327)	(0.4996)	12.42	0.77	50.59
Nd(IIII) :L (-)Asn	0.7880	2.7955	2.8478	3.1602	0.4565	11.27	9.96	52.30
	(0.9666)	(2.7856)	(3.0601)	(2.9124)	(0.5951)	11127	7.70	02.00
4. H_2O : DMF	0.0010	1.0200	2 40 41	10(70	0.5002	1	1	
Nd(IIII)	0.9912	4.0309	3.4061	4.2672	0.5803	15.61	16.84	65.75
	1 0247	4 1328	3 5283	4 3873	0 5923			
Nd(IIII) : L(-)Asn	(1.3913)	(4.1126)	(3.9626)	(3.8789)	(0.8790)	16.13	16.95	67.99
5. H ₂ O:CH ₃ CN:CH ₃ C)H	(11120)	(01) 020)	(510707)	(010770)			
	0.8659	2.8837	2.5641	3.0137	0.4203	11.04	11.01	47.70
Nd(IIII)	(0.9691)	(2.8780)	(2.8072)	(2.7340)	(0.6103)	11.26	11.61	47.72
Nd(IIII) ·I (_)Asn	0.9413	2.8970	2.5676	3.0811	0.4566	10.47	13 56	47 74
	(1.0193)	(2.8927)	(2.8193)	(2.7926)	(0.6621)	10.47	15.50	77.77
6.H ₂ O:CH ₃ CN:C ₄ H ₈ O ₂								
Nd(IIII)	0.8962	2.9919	2.3747	3.0180	0.4706	10.45	15.16	44.77
	(1.0360)	(2.9842)	(2.6577)	(2.6915)	(0.6857)			
Nd(IIII) :L (-)Asn	0.9943	3.0046	2.4456	3.0543 (2.7482)	(0.4/4/)	10.37	15.49	45.72
7 H ₂ O·CH ₂ CN·DME	(1.0348)	(3.0013)	(2.7133)	(2.7402)	(0.7003)			
7. 1120.0113010.Divit	0 9470	4 0751	2 9664	4 1250	0 4493			
Nd(IIII)	(1.3124)	(4.0549)	(3.5137)	(3.4899)	(0.8361)	15.89	17.33	59.49
	0.9533	4.0904	3.2151	4.2145	0.4669	16.50	15 71	(2.2.1
Nd(IIII) : L(-)Asn	(1.3104)	(4.0708)	(3.7190)	(3.6289)	(0.8168)	16.58	15.71	63.24
8. H ₂ O:CH ₃ OH:C ₄ H ₈	O ₂							
Nd(IIII)	0.8447	2.9155	2.0480	3.1290	0.4654	8 14	19 39	41 16
110(1111)	(1.1004)	(2.9014)	(2.4738)	(2.6359)	(0.7750)	0.14	17.57	41.10
Nd(IIII) : L(-)Asn	0.8914	2.9586	2.0496	3.1536	0.5091	7.73	20.93	40.92
	(1.1399)	(2.9449)	(2.4684)	(2.6689)	(0.8145)			
Nd(IIII)	(1.2397)	(3.4859)	(3.5882)	(3.5067)	(0.7941)	13.04	15.40	60.99
	1.0851	3.5146	3.4923	4.0891	0.5216	10.00		<i>ca</i> 10
Nd(IIII) :L (-)Asn	(1.2514)	(3.5054)	(3.8382)	(3.6904)	(0.7859)	13.62	14.02	65.49
10. H ₂ O:DMF:C ₄ H ₈ O	02							
Nd(IIII)	1.0959	3.7320	3.3228	4.9570	0.4845	10.91	22 50	68 60
	(1.5128)	(3.7090)	(4.0648)	(4.0993)	(1.0330)	10.71	22.39	00.00
Nd(IIII) ·I () Acr	1.1766	3.8734	3.5101	5.0814	0.5584	11 10	23 78	71 16
IND(IIII) :L (-)Asn	(1.5783)	(3.8513)	(4.2184)	(4.2626)	(1.0808)	11.19	23.10	/1.10

TABLE III COMPUTED AND OBSERVED VALUES OF OSCILLATOR STRENGTH ($P \times 10^6$) and judd-ofelt intensity parameters ($T_{\lambda} \times 10^{10}$; $\lambda = 2,4,6$) of ND(III) and ND(III) : L(-) asn (1:1) in the some selected binary (equimolar) and ternary organic solvent mixtures (equimolar).

Since, 4f-4f in fⁿ transitions are parity forbidden in accordance to electric dipole moment principle but are weakly allowed by the induced electric dipole moment. The weak induced electric dipole transition occurs as a result of interaction of central Nd(III) with the surrounding ligand field. The observed value of oscillator strengths of ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ transition is 75% more than the ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$ transitions in H₂O:CH₃OH, which reveals a strong sensitivity of transition. Thus, ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ transition is more sensitive to the environment for the interaction of Nd(III) with L(-) Asn complex. But, these results are contrarily to our previous report [38]. For these reasons, the present study reports that the transition ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ of Nd(III) with L(-) Asn has been found to be hypersensitive in the present coordination environment.

The magnitude of the spectral intensity parameters i.e., oscillator strengths and Judd-Ofelt intensity parameters can be of significance in order to predict the complexation and covalency. The orders of magnitude of oscillator strength values for the observed five transition bands are

$${}^{4}\mathrm{I}_{9/2} \rightarrow {}^{4}\mathrm{F}_{5/2} \! > {}^{4}\mathrm{G}_{5/2} \! > {}^{4}\mathrm{F}_{7/2} \! > {}^{4}\mathrm{G}_{7/2} \! > {}^{4}\mathrm{F}_{3/2}$$

Since, the values of oscillator strength of ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ in H₂O:CH₃OH are 28%, 78% and 93% more than H₂O:DMF, H₂O:C₄H₈O₂ and H₂O:CH₃CN respectively and they may be due to a strong interaction within the complex in this solvent. But, the values of oscillator strength are found to be more in DMF containing ternary solvent mixtures than the rest of the other ternary solvent mixtures [39]. One can see that the complex formed between the L(-) Asn and Nd(III) with high oscillator strength will be more stable as compared to the one with a lower oscillator strength. Obviously, the values of Judd-Ofelt intensity parameters T₂, T₄ and T₆ are becoming positives. Amid the three parameters, T₂ is most significant than T₄ and T₆ parameters of Nd(III):L(-) Asn complex [40]. Besides, the structure of ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ transition band of Nd(III):L(-) Asn complex is changed in H₂O:DMF as mentioned above. So, H₂O:DMF is considered to be good evidence for changes the symmetry of the complex in solution. For this reason, we have chosen the H₂O:DMF as a solvent in order to gain its hidden property of the formation of complex in this particular solvent by evaluating its thermodynamic parameters.

B. Thermodynamic Study

The equilibrium constant of Nd(III) with L(-) Asn in H₂O:DMF increases with increase in temperature which varies from 298K to 313K. Further, the thermodynamic parameters for the complexation of Nd(III) with L(-) Asn in H₂O:DMF are determined from the van't Hoff plot of ln K versus 1/T which gives a straight line as shown in Fig. 4.



Fig. 4 Plot of ln K versus $(1/T) \times 10^3$ for the complexation of Nd(III): L(-) Asn in H₂O: DMF (equimolar).

The standard enthalpy change, ΔH° and the standard entropy change, ΔS° are obtained from the slope and the intercept respectively. The changes in the standard enthalpy, entropy and free energy of the complexation process are summarized in Table IV.

TABLE IV THERMODYNAMIC PARAMETERS FOR THE BINDING OF ND(III) WITH L (-) ASN (1:1) IN $H_2O:DMF$ (EQUIMOLAR) AT DIFFERENT TEMPERATURES.

Temperature (K)	ΔH^{oa} (kJ mol ⁻¹)	$\frac{\Delta S^{ob}}{(J \text{ mol}^{-1} \text{ K}^{-1})}$	ΔG^{oc} (kJ mol ⁻¹)
298			-30.5411±6.6
303	0.0153 ± 0.45	102.4867 ± 1.48	-31.0536±6.6
308			-31.5660±6.6
313			-32.0784±6.6

a = Standard deviation of slope, b = Standard deviation of intercept, $c = Mean \pm standard$ deviation

The positive values of ΔH° and ΔS° indicate that the complexation of Nd(III):L (-) As is endothermic in nature with the increased randomness at the solution interface during the complexation. Further, the negative values of ΔG° at 298K, 303K, 308K and 313K show that the reaction of Nd(III) with L(-) As n in solution occurs spontaneously [41, 42].

IV. CONCLUSION

The results that have been discussed above confirm that the transition ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ might be a hypersensitive band when compared to other transition bands. The present work is more emphasis in the intensity parameters because it is more significant than the energy parameters. Thus, the magnitude of oscillator strength values in H₂O:CH₃OH and H₂O:DMF are found to be more than the other solvents and hence the complexation of Nd(III):L (-) Asn is more favored in these solvents. It may also be concluded that the complexation of Nd(III) with L(-) asparagine(monohydrate) might predominate as an inner sphere complexes in solution. Moreover, the positive values of enthalpy (Δ H °), entropy (Δ S °) and the negative values of free energy (Δ G °) indicate that the complexes can be expected to have potential application in absorption probe on calcium binding sites.

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