



A STUDY OF CHEMICAL SPECIATION ON NEODYMIUM- 1-(2-PYRIDYLAZO)-2- NAPHTHOL SYSTEMS IN CTAB, SDS AND TRITON X-100 AQUEOUS-MICELLAR MEDIA

ASHA MATHEW

¹Department of Chemistry, S.I.W.S. College, Wadala, Mumbai 400031, India.

ABSTRACT

Chemical speciation of binary complexes of Nd^{3+} with 1-(2-Pyridylazo)-2-naphthol (PAN) in varying concentrations in CTAB, SDS AND TRITON X-100 AQUEOUS-MICELLAR MEDIA are included has been studied pH metrically at an ionic strength of the solution in a total volume of 50.0 cm³,

0.1 mole dm⁻³ by the addition of sodium chloride solution. The temperature of the system was maintained at $30.0 \pm 0.10^\circ\text{C}$. The active forms of Nd^{3+} are ML , ML_2 and ML_3 for refined and confined using the computer programs SCPHD and MINQUAD75. The species distribution with pH at different solvent composition, plausible equilibria and structures of the species are also presented.

KEY WORDS: Chemical speciation, Neodymium, 1-(2-Pyridylazo)-2-naphthol (PAN), CTAB, SDS AND TRITON X-100, MICELLAR MEDIA, MINQUAD75.

INTRODUCTION:

When a metal ion is in contact with a ligand or several ligands, depending on their relative concentrations and other experimental conditions, there is a chance of formation of a number of species of diverse stoichiometry. Further, depending on the protonation equilibria of the ligand and pH of the solution, there is a possibility of formation of protonated and hydroxylated species in addition to simple complexes. As these species may be having overlapping equilibria, there is a probability of presence of several co-existing species with different physical and chemical properties at any arbitrarily selected set of experimental conditions. In analytical determinations of metal ions, the experimental conditions must therefore be set so that a particular species of interest that is sensitive to the probe forms to a maximum extent and represents the total concentration of metal ion of interest. Selection of experimental conditions for analytical determinations without a prior knowledge of species distribution leads to unexpected/ inaccurate estimations. Therefore, to get the required information regarding the nature and extent of formation of various species as a function of pH, chemical speciation study is a prerequisite for any analytical determination. Hence, in this chapter the results of the speciation study of the binary systems of 1-(2-Pyridylazo)-2-naphthol (PAN) with lanthanide, Nd^{3+} , in aqueous micellar media are included.

PAN exhibits excellent complexing ability for heavy and transition metal ions, and its analytical applications in the spectrophotometric determination of the metals are well established. Several studies have been performed to determine the stoichiometry of the PAN metal chelates. Shibata proposed a ratio of 1:2 for most of the lanthanide: PAN complexes¹. Later on, Rao et al.² reported a 1:3 ratio for some lanthanide complexes based on IR, UV and visible absorption spectra, electrical conductivity and magnetic susceptibility data in solid state. In these complexes, PAN appears to function as a bidentate ligand, bonding through the oxygen of the –OH group and azo nitrogen (linked to the pyridine ring). Dwyer et al.³ and Gao et al.⁴ have reported PAN as a powerful chelating agent that reacts with over 30 elements forming highly coloured complexes. In most of these complexes, PAN appears to behave as a tridentate ligand with the heterocyclic nitrogen, the nitrogen of the azo group which is farthest from the pyridine ring and the hydroxyl oxygen as bonding centres.

Danuta M. Czakis-Sulikowska et al.⁵⁻⁸ determined the composition and conditional complex formation constants of PAN (LH) with Ln^{3+} ions in methanol-water, ethanol-water, n-propanol-water and iso-propanol-water solutions by spectrophotometric method. The composition of the complexes formed was found to be 1:1 (LnL^{2+}). The formation constants were found to increase with increase in organic solvent composition. Their values were also found to depend on the nature of the organic solvent and decrease in the order of methanol > ethanol > isopropanol > n-propanol. These trends were attributed to the change in dielectric constant of the medium.

Safari et al.⁹ spectrophotometrically determined the composition and formation constants of complexes of Ni^{2+} , Co^{2+} and Zn^{2+} (M) metal ions with PAN (L) in methanol, acetonitrile and dimethyl sulfoxide. The results revealed that the formed complexes were of ML_2 type and their stabilities were in the order $\text{Ni}^{2+} < \text{Zn}^{2+} < \text{Co}^{2+}$ for all the solvents. The values of the thermodynamic parameters (ΔH^0 , ΔS^0 and ΔG^0) for complexation reactions were also calculated from the temperature dependence of the stability constants.

Formation of Tm (III) complex with PAN(HL) in aqueous-methanol mixtures (50 and 75% v/v) using a spectrophotometric method was studied by Kuznik et al.¹⁰ The equilibrium constant for the formation of TmL^{2+} species was calculated.

The ionization constant of PAN and the formation constants of its complexes with ZrO^{2+} , Nb^{5+} , Pd^{2+} , and Cd^{2+} were investigated by Moustafa Mahmoud¹¹ using a potentiometric method. The stoichiometry of the complexes formed was established using spectrophotometric and conductometric titrations. The complexes were isolated in solid state and were characterized by elemental analysis, TGA and IR spectra. The ligand was found to act as a bidentate bonding through the Naphtholic oxygen and nitrogen of the –N-N- group.

Rao et al.¹² reported the formation of 1: 3 PAN: lanthanide complexes in water-ethanol mixtures. The formation constants of the complexes were determined spectrophotometrically and were found to lie in the range 13.71-15.47.

Fedin et al.¹³ established a relation between instability constants of metal complexes and the electric field strength (E) of the coordinating cation of the complexes of 1-(2-pyridylazo)-2-naphthol, 1-(2-thiazolylazo)-2-naphthol, Xylenol Orange, pyrocatechol violet, and Chromazurol S. The relation $\text{pK}_i = a + b \cdot \text{Nd}(E)$ was derived on the basis of an electrostatic model of metal ion-ligand interaction.

Proton association constants of PAN and its metal–ligand stability constants with Indium (III) in 50% (v/v) aqueous-dioxane medium were reported by Sarin et al.¹⁷ The step-wise formation constants, $\log K_1$ and $\log K_2$ were 12.19 and 10.57, respectively.

Toropova et al.¹⁴ reported the formation constants of Al (III) complexes of PAN in 50% aqueous ethanol. The formation constants were determined polarographic ally at 25°C and ionic strength of 0.1M.

The molar absorptivity and formation constant of 1:2 Ti (IV)-PAN complex were reported by Betteridge et al.¹⁵ The absorption maximum at 582 nm was used for the spectrophotometric determination of the metal ion.

The stability constants of the complexes of Ni(II), Cu(II) and Hg(II) with the PAN reagent, dissolved in chloroform were determined directly from spectrophotometric measurements; they were: $\log \beta_{av} = 24.12$, 24.00 and 21.88 for Hg(II), Cu(II) and Ni(II) respectively.

Escriche et al.¹⁶, reported the formation constant of Cd (PAN)₂ complex determined by a spectrophotometric method in a nonionic surfactant solution (polyoxyethylenenonyl phenol). The conditional formation constant obtained in 2% surfactant solution was 11.54.

Literature reports therefore, indicate that a thorough speciation study of metal ion-PAN equilibria was not carried out in spite of its importance in the selection of experimental conditions for analytical determination of metal ions. Further, in solution, depending on the pH, PAN may exist in LH²⁺, LH and L⁻ forms. Therefore, there is a chance of formation of protonated and hydroxylated species in addition to simple complexes. The formation constants obtained without considering all these equilibria are not reliable. Therefore, the author has taken up a study on speciation of Nd³⁺-PAN systems in aqueous-micellar systems without adding any organic solvent.

EXPERIMENTAL

The titrimetric data were obtained with a calibrated ELICO (Model L1-120) pH-meter (readability 0.01) which can monitor the changes in H⁺ concentration. The pH meter was calibrated with 0.05 M potassium hydrogen phthalate in acidic region and 0.01 M borax solution in basic region. The glass electrode was equilibrated in a well-stirred PG-water mixture containing inert electrolyte.

The investigation of Nd³⁺-PAN systems in cationic, anionic, and neutral micellar media utilized the Calvin-Wilson titration technique²⁰. The data acquisition process involved titrating a mixture consisting of hydrochloric acid, metal ion, and PAN with a standard solution of sodium hydroxide. The surfactant concentration was adjusted to 0.02 mole dm⁻³, and the ionic strength of the solution in a total volume of 50.0 cm³ was maintained by adding sodium chloride solution. The temperature was controlled at 30.0 ± 0.10°C by circulating thermostatted water through the titration vessel's annular space. The metal-to-ligand concentration ratio varied (1:1, 1:2, and 1:3) in different experiments, ensuring a comprehensive exploration of the system. To verify data reproducibility, 2 to 3 independent titrations were conducted for each system. The calculation of stability constants employed 90 to 160 data points, depending on the specific metal ion and ligand.

RESULTS AND DISCUSSION FROM THE CHEMICAL MODELING STUDY ON Nd³⁺ -PAN SYSTEMS:

The results of the author's studies on the proton-ligand equilibria of PAN as discussed¹ showed the formation of LH²⁺, LH and L⁻ type of species (Figure 4.1) in solution.

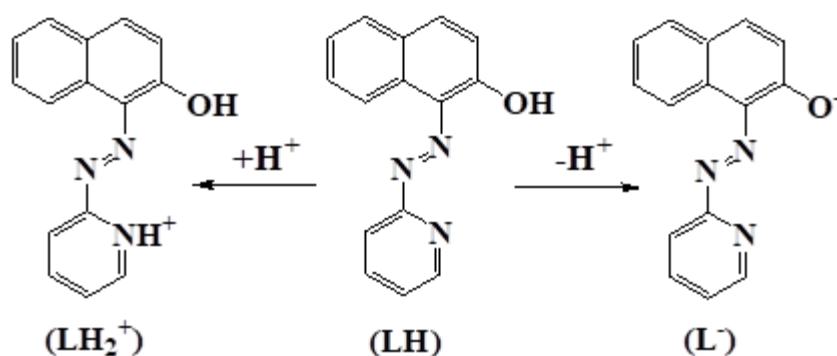
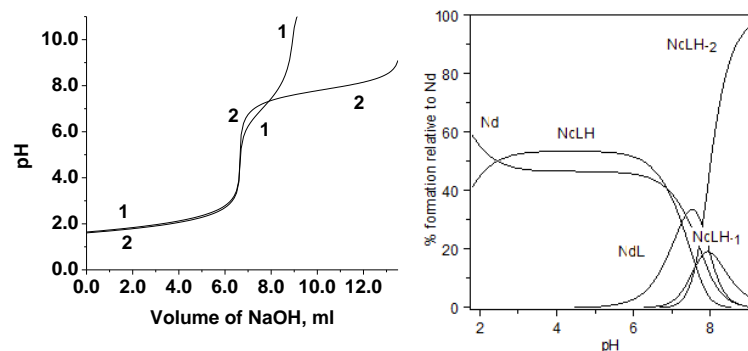


Figure 4.1: Protonated and deprotonated form of PAN (LH)

Hence, there is a possibility of formation of a variety of coexisting mononuclear Nd³⁺ -PAN complexes in protonated, unprotonated and hydroxylated forms. Therefore, the ligand may be bound to metal ions in different states of protonation, thus enabling the properties of their complexes to be modulated by the degree of deprotonation.

The experimental data acquired for Nd³⁺ -PAN systems of 1:1, 1:2 and 1:3 (M: L) concentration compositions were first subjected to analysis by classical procedures^{18, 19}. The experimental and simulated titration curves for PAN-metal ion systems in CTAB, SDS and Triton X-100 micellar media are shown in Figures 4.2a to 4.19a. suitable chemically plausible models were prepared for refinement using the Miniquad-75 program. The best-fit models obtained for all the Nd³⁺ -PAN systems are tabulated in Tables 4.1 to 4.3. Tables contain the composition and formation constants of all the species converged along with their standard deviations and other statistical parameters used for the selection of best-fit model.



a. 1. Simulated titration curve
2. Experimental titration curve

b. Species distribution diagram

[PAN] = 0.01004 mol dm⁻³

[HCl] = 0.02874 mol dm⁻³

Total Volume = 50.0 cm³

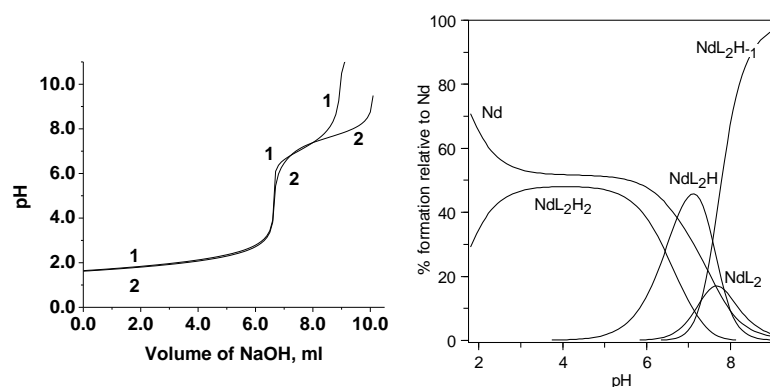
Temp = 30.0 ± 0.1°C

[Nd (III)] = 0.0100 mol dm⁻³

[NaOH] = 0.21603 mol dm⁻³

I = 0.1 mol dm⁻³ NaCl

Figure 4.2: Nd (III) - PAN SYSTEM (1:1) in CTAB



V. 1. Simulated titration curve
2. Experimental titration curve

b. Species distribution diagram

[PAN] = 0.00997 mol dm⁻³

[HCl] = 0.02874 mol dm⁻³

Total Volume = 50.0 cm³

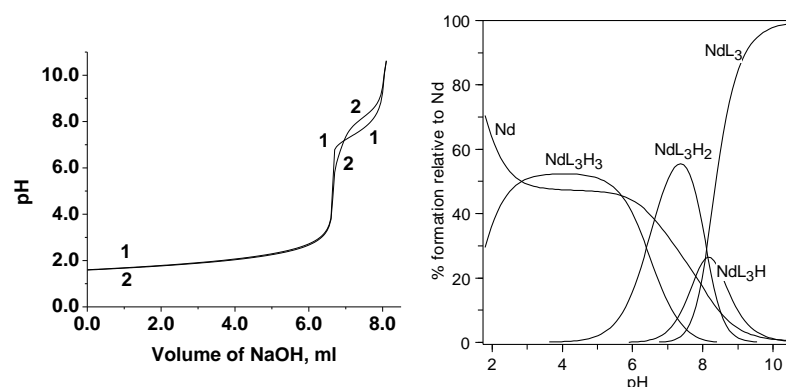
Temp = 30.0 ± 0.1°C

[Nd (III)] = 0.0050 mol dm⁻³

[NaOH] = 0.21603 mol dm⁻³

I = 0.1 mol dm⁻³ NaCl

Figure 4.3: Nd (III) - PAN SYSTEM (1:2) in CTAB



a. 1. Simulated titration curve
2. Experimental titration curve

b. Species distribution diagram

[PAN] = 0.00600 mol dm⁻³

[HCl] = 0.02874 mol dm⁻³

Total Volume = 50.0 cm³

Temp = 30.0 ± 0.1°C

[Nd (III)] = 0.0020 mol dm⁻³

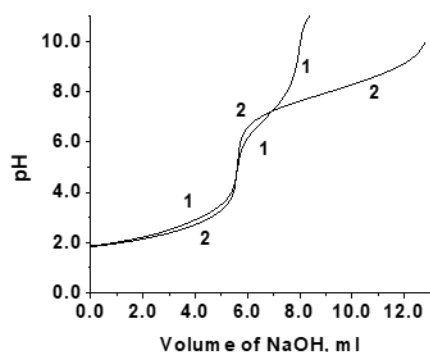
[NaOH] = 0.21603 mol dm⁻³

I = 0.1 mol dm⁻³ NaCl

Figure 4.4: Nd (III) - PAN SYSTEM (1:3) in CTAB

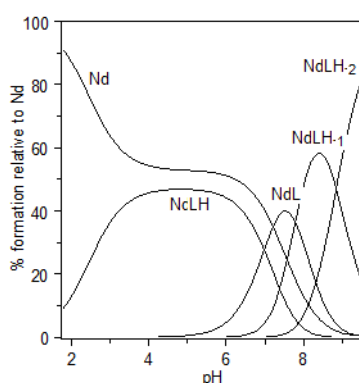
Table 4.1: Best fit chemical models of PAN- Ln^{3+} metal ion systems in 0.02M CTAB medium at 303.0 K and ionic strength, $I = 0.1 \text{ mol dm}^{-3}$ (NaCl) (SD= Standard Deviation in the least significant digit)

Metal ion	Composition (M: L)	Species mlh	Log β_{mlh} (SD) (in CTAB)	Statistical parameters
Nd^{3+}	1:1	011	10.41	$U/\text{NP} = 8.149 \times 10^{-8}$
		012	12.24	$\chi^2 = 10.14$
		111	12.80 (8)	$R = 0.0133$
		110	5.55 (3)	Skewness= 0.01
		11-1	-2.43 (3)	Kurtosis= 3.64
		11-2	-10.02 (2)	
	1:2	011	10.41	$U/\text{NP} = 1.505 \times 10^{-8}$
		012	12.24	$\chi^2 = 10.07$
		122	25.37 (17)	$R = 0.0201$
		121	18.93 (5)	Skewness= 0.71
		120	11.09 (15)	Kurtosis= 6.03
		12-1	3.79 (18)	
	1:3	011	10.41	$U/\text{NP} = 3.580 \times 10^{-10}$
		012	12.24	$\chi^2 = 7.20$
		133	38.92 (5)	$R = 0.0035$
		132	32.52 (9)	Skewness= 0.75
		131	24.37 (4)	Kurtosis= 5.04
		130	16.30 (7)	



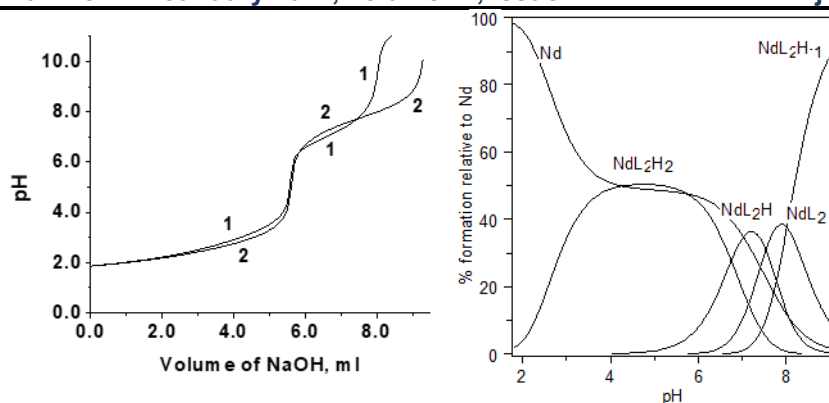
a. 1. Simulated titration curve

2. Experimental titration curve

[PAN] = $0.00998 \text{ mol dm}^{-3}$ [HCl] = $0.02292 \text{ mol dm}^{-3}$ Total Volume= 50.0 cm^3 Temp= $30.0 \pm 0.1^\circ\text{C}$ 

b. Species distribution diagram

[Nd (III)] = $0.0100 \text{ mol dm}^{-3}$ [NaOH] = $0.2044 \text{ mol dm}^{-3}$ $I = 0.1 \text{ mol dm}^{-3} \text{NaCl}$ **Figure 4.20:** Nd (III) - PAN SYSTEM (1:1) in SDS



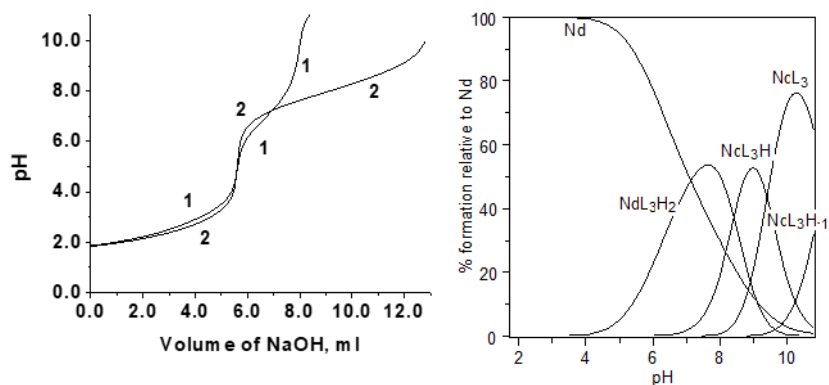
a. 1. Simulated titration curve

b. Species distribution diagram

2. Experimental titration curve

[PAN] = 0.00998 mol dm⁻³[Nd (III)] = 0.0050 mol dm⁻³[HCl] = 0.02292 mol dm⁻³[NaOH] = 0.2044 mol dm⁻³Total Volume = 50.0 cm³

Temp = 30.0 ± 0.1°C

I = 0.1 mol dm⁻³ NaCl**Figure 4.21:** Nd (III) - PAN SYSTEM (1:2) in SDS

a. 1. Simulated titration curve

b. Species distribution diagram

2. Experimental titration curve

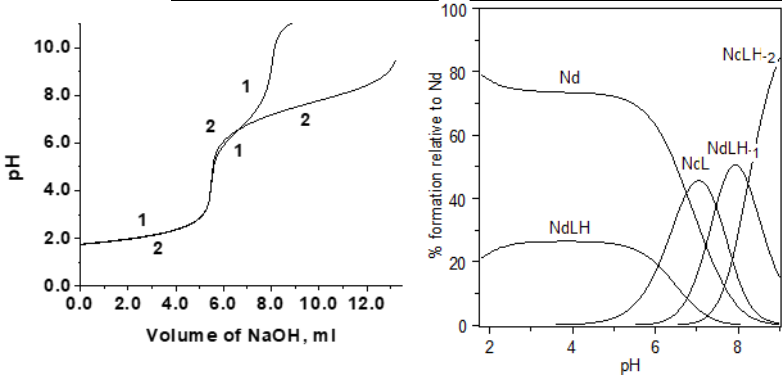
[PAN] = 0.00600 mol dm⁻³[Nd (III)] = 0.0020 mol dm⁻³[HCl] = 0.02292 mol dm⁻³[NaOH] = 0.2044 mol dm⁻³Total Volume = 50.0 cm³

Temp = 30.0 ± 0.1°C

I = 0.1 mol dm⁻³ NaCl**Figure 4.22:** Nd (III) - PAN SYSTEM (1:3) in SDS

Table 4.2: Best fit chemical models of PAN- Ln^{3+} metal ion systems in 0.02M SDS medium at 303.0 K and ionic strength, $I = 0.1 \text{ mol dm}^{-3}$ (NaCl) (SD= Standard Deviation in the least significant digit)

Metal ion	Composition (M: L)	Species mlh	Log β_{mlh} (SD) (in SDS)	Statistical parameters
Nd^{3+}	1:1	011	11.79	$U/NP = 1.528 \times 10^{-8}$
		012	14.75	$\chi^2 = 12.71$
		111	14.02 (7)	$R = 0.018$
		110	7.04 (5)	Skewness= -0.11
		11-1	-0.749 (2)	Kurtosis= 4.12
		11-2	-9.59 (10)	
	1:2	011	11.79	$U/NP = 1.422 \times 10^{-8}$
		012	14.75	$\chi^2 = 9.25$
		122	28.23 (11)	$R = 0.0239$
		121	21.48 (9)	Skewness= -1.50
		120	13.95 (5)	Kurtosis= 6.28
		12-1	5.94 (8)	
	1:3	011	11.79	$U/NP = 1.179 \times 10^{-8}$
		012	14.75	$\chi^2 = 3.49$
		132	35.84 (12)	$R = 0.0187$
		131	27.42 (14)	Skewness= -0.13
		130	18.02 (15)	Kurtosis= 2.74
		13-1	6.92 (8)	



a. 1. Simulated titration curve

2. Experimental titration curve

$[\text{PAN}] = 0.01003 \text{ mol dm}^{-3}$

$[\text{HCl}] = 0.02104 \text{ mol dm}^{-3}$

Total Volume= 50.0 cm^3

Temp= $30.0 \pm 0.1^\circ\text{C}$

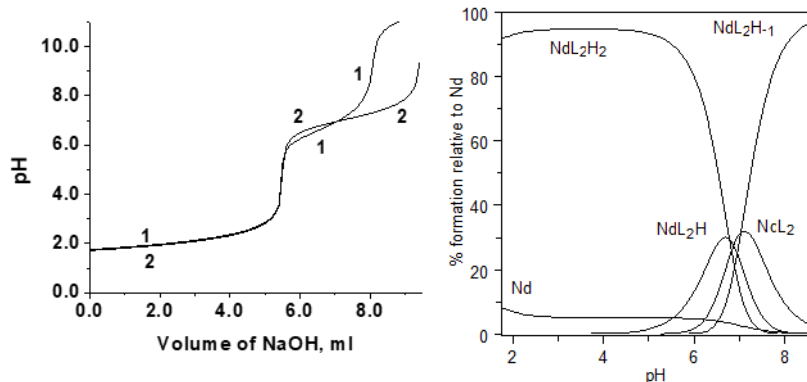
$I = 0.1 \text{ mol dm}^{-3}\text{NaCl}$

b. Species distribution diagram

$[\text{Nd (III)}] = 0.0100 \text{ mol dm}^{-3}$

$[\text{NaOH}] = 0.1916 \text{ mol dm}^{-3}$

Figure 4.38: Nd (III) - PAN SYSTEM (1:1) in T X-100



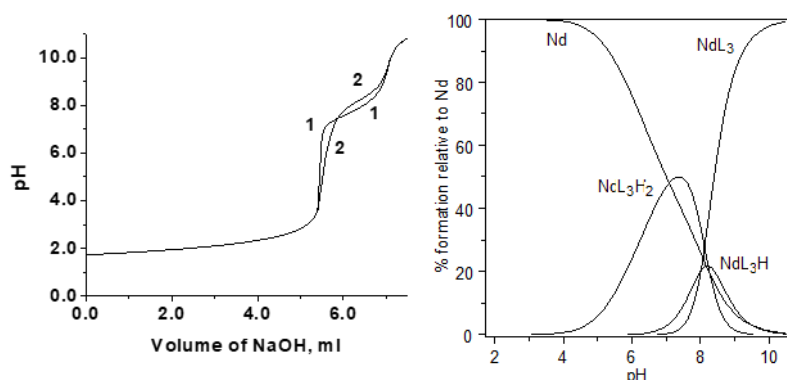
a. 1. Simulated titration curve

b. Species distribution diagram

2. Experimental titration curve

[PAN] = 0.00998 mol dm⁻³[Nd (III)] = 0.0050 mol dm⁻³[HCl] = 0.02104 mol dm⁻³[NaOH] = 0.1916 mol dm⁻³Total Volume = 50.0 cm³

Temp = 30.0 ± 0.1°C

I = 0.1 mol dm⁻³ NaCl**Figure 4.39:** Nd (III) - PAN SYSTEM (1:2) in T X-100

a. 1. Simulated titration curve

b. Species distribution diagram

2. Experimental titration curve

[PAN] = 0.00600 mol dm⁻³[Nd (III)] = 0.0020 mol dm⁻³[HCl] = 0.02104 mol dm⁻³[NaOH] = 0.1916 mol dm⁻³Total Volume = 50.0 cm³

Temp = 30.0 ± 0.1°C

I = 0.1 mol dm⁻³ NaCl**Figure 4.40:** Nd c(III) - PAN SYSTEM (1:3) in TX-100**Table 4.3:** Best fit chemical models of PAN- Nd³⁺ metal ion systems in 0.02M TX-100 medium at 303.0 K and ionic strength, I = 0.1 mol dm⁻³ (NaCl)

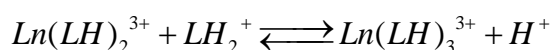
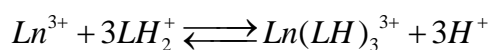
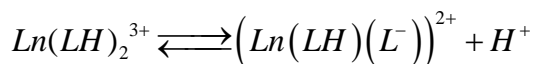
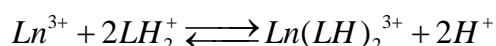
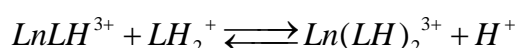
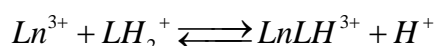
(SD= Standard Deviation in the least significant digit)

Metal ion	Composition (M: L)	Species mlh	Log β _{mlh} (SD) (in TX-100)	Statistical parameters
Nd ³⁺	1:1	011	11.96	U/NP = 1.896 X10 ⁻⁸
		012	13.42	χ ² = 31.49
		111	13.65 (2)	R=0.0201
		110	7.58 (4)	Skewness= -0.07
		11-1	0.112 (2)	Kurtosis= 3.89
		11-2	-8.13 (3)	
	1:2	011	11.96	U/NP = 7.348 X10 ⁻⁹
		012	13.42	χ ² = 26.02
		122	28.73 (10)	R=0.016
		121	21.95 (8)	Skewness= -0.07
		120	15.08 (6)	Kurtosis= 3.38
		12-1	8.05 (2)	
		011	11.96	U/NP = 9.173 X10 ⁻⁹
		012	13.42	χ ² = 11.36

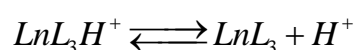
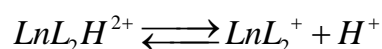
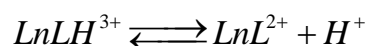
	1:3	132	36.41 (11)	R= 0.015
		131	28.18 (9)	Skewness= -0.14
		130	20.17 (5)	Kurtosis= 4.07

The study considered the formation of various Neodymium hydroxide species, such as $\text{Nd}(\text{OH})^{2+}$, $\text{Nd}(\text{OH})^{2+}$, and $\text{Nd}(\text{OH})_3$. These species are formed as a result of the interaction of lanthanides with hydroxide ions in the solution. models that included equilibria related to the formation of lanthanide hydroxide species were used. the negative formation constant after refinement suggests a challenge in accurately determining the stability constants of these species. The inclusion of lanthanide complexes of the form $\text{NdL}_i\text{H}_{-h}$ (where L represents a ligand) resulted in a good fit in most systems. This indicates that the formation of hydroxylated complexes occurs at higher pH, specifically in basic (alkaline) conditions. NdLH Type of Species forms when PAN likely acts as a monodentate or bidentate ligand through nitrogen atoms, excluding the -OH group. NdLH species are present in solution at a pH below approximately 6.0. At higher pH levels, a different species, NdL , is formed, where the -OH group of PAN likely participates in bonding through deprotonation. At even higher pH, NdLH_{-1} and NdLH_{-2} species appear in the solution, possibly due to hydrolysis of the previous species. Various chemical models, including NdL_2H_2 , NdL_2H , NdL_2 , $\text{NdL}_2\text{H}_{-1}$, and

$\text{NdL}_2\text{H}_{-2}$, were tested to fit the experimental data. Species Distribution Diagrams show the percentage of formation of different species for various lanthanide ions in different media (CTAB, SDS, Triton X-100) at a 1:2 metal to ligand concentration ratio. Due to the possibility of lanthanide ions exhibiting higher coordination numbers, potentiometric titrations with a 1:3 metal to ligand concentration ratio were conducted to explore the formation of species where the metal ion is bonded to three PAN molecules. Best-fit models suggested the formation of NdL_3H_3 , NdL_3H_2 , NdL_3H , and $\text{NdL}_3\text{H}_{-1}$ species. The neutral NdL_3 species reached a maximum at pH 10.0 to 10.2. The influence of micellar media on complexation equilibria was explored. The order of formation constants was $\beta_{\text{mlh}}(\text{CTAB}) \ll \beta_{\text{mlh}}(\text{SDS}) < \beta_{\text{mlh}}(\text{Triton X-100})$. This order suggests that different types of surfactants (cationic, anionic, neutral) impact the complexation differently. The ligand's solubilization in different regions of aggregates alters properties through electrostatic, hydrophobic, and medium effects. In CTAB (cationic) medium, the formation constants are low, attributed to electrostatic repulsion between cationic head groups of CTAB micelles and Nd^{3+} ions. In SDS (anionic) medium, formation constants are high, indicating a more favorable environment for complex formation. Anionic micelles favor the formation of lanthanide-PAN complexes due to electrostatic attractive forces.



etc



etc

There is a likelihood of forming ionic pairs between cationic species and anionic head groups of SDS. These ternary species further stabilize binary complexes. There is a competition between the ligand (PAN) and anionic surfactant head groups for metal ions. Depending on the relative importance of the above factors, this competition may lead to a decrease in the apparent formation constant of complexes. For Nd^{3+} -PAN systems, positive effects, such as electrostatic attraction and the formation of stabilized ternary species, seem to dominate. This results in an overall increase in formation constants. Triton X-100, being a non-ionic surfactant, affects complex formation through polarity and hydrophobic factors. The micelle formed by Triton X-100 consists of a hydrophobic core and hydrated Polyoxyethylene groups in the palisade layer. PAN, having a hydroxyl group, may interact with oxyethylene groups through hydrogen bonding and be solubilized between the core and palisade layer. The

speciation studies recommend the neutral NdL_3 type of species for the analytical determination of lanthanide ions. Triton X-100 micellar system is considered the best due to relatively high formation constants of the species. Experimental conditions, such as pH and relative concentrations of metal ions and PAN, must be optimized to ensure that the total metal ion is in the NdL_3 form.

CONCLUSION

1. Lanthanides exhibit hydrolysis in solution, leading to the formation of hydroxide species.

Equilibrium models were employed to study the formation of lanthanide hydroxide species, but the determination of their stability constants posed challenges, including negative values during refinement. 2. The presence of ligands affects the detection of free, uncomplexed metal ions required for the formation of metal hydroxide species, especially at higher pH. Despite these challenges, the inclusion of lanthanide hydroxylated complexes in the form of $\text{LnL}_i\text{H}_{-i}$ resulted in a good fit, indicating the occurrence of hydroxylated complexes at higher, basic pH levels. 3. Two main types of species, LnLH and LnL , form at lower and higher pH, respectively. The appearance of LnLH_{-1} and LnLH_{-2} at even higher pH suggests potential hydrolysis of the preceding species. 4. Micellar media, including CTAB (cationic), SDS (anionic), and Triton X-100 (non-ionic), were investigated for their influence on complexation equilibria. Anionic micelles (SDS) were found to favour complex formation due to electrostatic attractive forces and the potential formation of ternary species. In non-ionic micelles (Triton X-100), the structure and properties of the micelle, particularly the solubilization of PAN, played a crucial role in stabilizing complexes. 5. Triton X-100 micellar systems demonstrated relatively high formation constants, making them favorable for spectrophotometric determination of lanthanides. The order of formation constants in different micellar media ($\beta_{\text{mlh}}(\text{CTAB}) \ll \beta_{\text{mlh}}(\text{SDS}) < \beta_{\text{mlh}}(\text{Triton X-100})$) highlights the varying impacts of cationic, anionic, and non-ionic surfactants on complexation.

References

- 1.S. Shibata, "Chelates in Analytical Chemistry"; Marcel Dekker, Inc.;1972, Chapter- 4; pp101-108.
2. I.M.Rao, D. Satyanarayana, and U.Agarwala, *Bull. Chem. Soc. Jap.*, 52(2) (1979) pp 588-591.
- 3.F.P.Dwyer, and D.P.Mellor, "Chelating Agents & Metal Chelates", Academic Press: London; 1964; Chapter 1; 1-50.
4. J.Gao, J.Kong and G.Bai, *Talanta*, 40(2) (1993) pp 195-200.
5. Danuta M. Czakis-Sulikowska and Anna Malinowska, "Complex formation of certain rare earth metals with 1-(2-pyridylazo)-2-naphthol (PAN) in alcohol-water solutions", *Monatshefte für Chemie*, 119(1988) pp 677-681.
6. Danuta M. Czakis-Sulikowska and Anna Malinowska, "Complex formation studies on Ho(III) and Lu(III) with 1-(2-pyridylazo)-2-naphthol (PAN) in alcohol-water solutions", *Monatshefte für Chemie*, 117(1986)pp 437-444.
7. Danuta M. Czakis-Sulikowska and Anna Malinowska, *Acta Chim Hung*, 118(1985) pp 121-129.
8. Danuta M. Czakis-Sulikowska and Anna Malinowska, *Polish J.Chem*, 55(1981)963.
9. Z. Safari, M.B. Gholivand and L. Hosseinzadeh, 'Spectrophotometric study of complex formations between 1-(2-pyridylazo)-2-naphthol (PAN) and some metal ions in organic solvents and the determination of thermodynamic parameters', *Spectrochimica Acta Part A*, 78 (2011) 1606–1610.
10. B. Kuznik and A.Mlinowaska, "Solvent extraction of Rare earth metal ions with 1-(2-pyridylazo)-2-naphthol (PAN)-V-Complex formation and distribution equilibria of Thulium(III) with PAN", *Monatshefte für Chemie*, 118(1987) pp 1325-1333.

11. M. Moustafa Mahmoud, "Studies of the Oxozirconium (2+), Niobium (5+), Palladium (2+) and Cadmium (2+) chelates with 1-(2-pyridylazo)-2-naphthol", *Delta Journal of Science* 16(2)(1992) pp 93-109
12. I.M.Rao and D. Satyanarayana, "Spectrophotometric studies on lanthanide complexes with 1-(2-pyridylazo)-2-naphthol(PAN) in water-ethanol medium", *J.Ind. Chem.Soc.*, 57(11) (1980) pp 1132-1134.
13. A.V. Fedin and M.Z.Yampolskii, "Stability constants of complexes of certain metals with organic compounds", *ZhurnalNeorganicheskoiKhimii*, 25(11) (1980) pp 2883-88.
14. V.F.Toropova, G.K. Budnikov and V.N. Maistrenko, "Polarography of complexes of metals with substituted azo compounds-V: Complexing of aluminum with 1-(2-pyridylazo) resorcinol, 1-(2-pyridylazo)-2-naphthol (PAN) and 1-(2-thiazolylazo)-2-naphthol", *ZhurnalObshcheiKhimii*, 45(7) (1975) pp 1570-74.
15. D. Betteridge, D. John and F. Snape, "Pyridylazonaphthols and pyridylazophenols as analytical reagents. IV. Formation of complexes with titanium(IV)", *Analyst (U.K.)* 98(1973) pp 520-24.
16. J.MedinaEscriche, M.Llobat Estelle and F. BoschReig, "Spectrophotometric determination of Cadmium with 1-(2-pyridylazo)-2-naphthol and nonionic surfactants", *Talanta*, 30(12) (1983) pp. 915-918.
17. R.Sarin and K.N. Munshi, "Potentiometric study of the complexes of indium (III) with some azo dyes", *J.Ind.Chem.Soc.*, 55(5)(1978) pp 512-513.
18. H. M. Irving, H. S. Rossotti, "Methods for Computing Successive Stability Constants from Experimental Formation Curves". *J. Chem. Soc.* (1953) 3397–3405.
19. H. M. Irving, H. S. Rossotti, "The Calculation of Formation Curves of Metal Complexes from pH-Titration Curves in Mixed Solvents", *J. Chem. Soc.* (1954) 2904–2910.
20. M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, 67 (1945) 2003.