Asian Journal of Chemistry Vol. 14. No. 1 (2002), 506–508

NOTE

Polarographic Study on Binary and Ternery Complexes of Nd(III) with 2-2-Bipyridyl and Urea†

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Polarographic measurements have been used to determine the overall formation constant of simple and mixed complexes of Nd(III) with urea and 2-2-bipyridyl at 25 ± 0.1°C. Polarograms of Nd(III)-urea-bipyridyl system at pH 2.40 ± 0.02 in aqueous medium have been used to study the complexes. The reduction of metal and its binary and ternary complexes is found to be reversible and diffusion controlled. Three mixed ligand species $[Nd(Bip)(Ur)]^{3+}$, $[Nd(Bip)(Ur)_2]^{3+}$ and $[Nd(Bip)_2(Ur)]^{3+}$ have been found *in situ* and their stability constants were computed. The values are log B_{11} = 4.90, log B_{12} = 5.26 and log B_{21} = 6.07. The mixing constant $K_m = B_{11}/\sqrt{B_{20}B_{02}}$ and stabilization constant log K_s = log K_m − log 2 are computed; the log values are found to be 1.02 and 0.72 respectively. The positive values of mixing constant and stabilization constant proved that mixed complexes are more stable than simple binary complexes. Disproportion constant for reaction

$$2[Nd(Bip)(Ur)]^{3+} \rightleftharpoons [Nd(Bip)_2]^{3+} + [Nd(Ur)_2]^{3+}$$

was found to be −1.14, The −ve value clearly indicates preferential tendency of Nd(III) to form mixed complex species.

Key words: Polarography, Nd(III), complexes.

The polarographic study of metal complexes in its own right has recognized a specialized field. Chitle and Pitre[1] have reported binary complexes of Ce(III), Pr(III) and Nd(III) with amino acids. Lavale *et al.*[2] reported Nd(III) complexes with crotonic and acrylic acid only. However, literature lacks references on the ternary complexes of rare earth metals using polarographic measurements. This prompted us for the present investigation using polarographic measurements. Possible mechanisms of electron transfer and complex formation have been discussed in detail. Metal-ligand interaction, preferential formation of mixed complexes and tendency of various complexes to add and substitute is also recorded.

All the chemicals used were of AnalaR grade and their solutions were prepared in bidistilled water. The solution of 2-2′-bipyridyl was prepared in diluted HCl. The ionic strength was kept constant at μ = 1.0 adjusting with KCl solution. 0.01% solution of gelatin was used as maximum suppressor. The concentration of Nd(III) was kept constant at 1 mmol dm^{-3} and pH was fixed at 2.40 ± 0.02.

†Paper presented at 19th ICC conference, Kevempu University, Shimoga, 27–29 Nov. 2000.

An automatic Elico-lab DC recording polarograph model Cl-25D with recorder model LR-101 P was used to record the polarograms. The DME characteristic was found to be $m^{2/3}t^{1/6} = 2.316\ mg^{2/3}\ sec^{-1/2}$. All measurements were made at 25 ± 0.1°C.

Nd(III) and its complexes gave three-electron reversible and diffusion controlled wave in 1.0 mol dm^{-3} KCl at pH = 2.40 ± 0.02. The slopes of linear plots of $\log \frac{1}{i_d - i}$ *vs.* E_{de} were of the order 20 ± 1 mV and the plots of i_d *vs.* th_{eff} were linear passing through origin.

Binary Systems: Deford and Hume's method[3] was applied to evaluate overall stability constants of binary complexes with each ligand. The cathodic shift in $E_{1/2}$ coupled with decrease in diffusion current with increasing ligand concentration indicated the formation of complexes of 2,2′-bipyridyl and urea each.

Nd(III)-bipyridyl system: The plot of $-(E_{1/2})_C$ *vs.* $\log C_L$, where C_L is the concentration of ligand is found to be a smooth curve with three segmets, showing the existence of 1 : 1, 1 : 2, 1 : 3 complex species. The Deford and Hume's treatment revealed $\log B_{10} = 3.10$, $\log B_{20} = 4.32$ and $\log B_{30} = 5.50$.

Nd(III)-Urea System: The concentration of urea was varied from 0.02 to 0.16 mol dm^{-3}. The negative shift in $E_{1/2}$ values revealed complex formation. Three complex species were detected with their overall stability constant $\log B_{01} = 1.17$, $\log B_{02} = 3.44$ and $\log B_{03} = 5.20$.

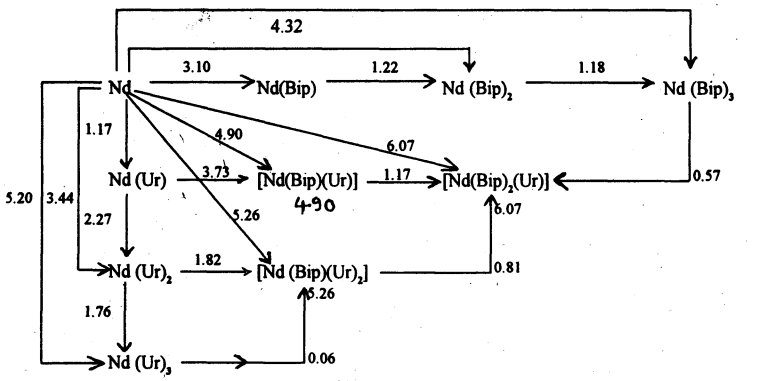
Nd(III)-Bipyridyl-Urea ternary system: Two concentrations of urea (0.1 and 0.2 mol dm^{-3}) were chosen for study of ternary complexes. The concentration of bipyridyl was varied from 0.0 to 0.1 mol dm^{-3}. $E_{1/2}$ shifted to more –ve values as compared to the shift obtained in presence of urea only, which revealed the formation of ternary complexes. The method of Schaap and McMaster[4] was used to determine the composition and values of stability constants. The polarographic characteristics and $F_{ij}(x)$ functions of the ternary complexes Nd(III) with bipyridyl and urea (fixed) have been reported in Tables 1 and 2. The functions A, B, C, D were evaluated by Leden-extrapolation method[5]. Three mixed species $[Nd(Bip)(Ur)]^{3+}$, $[Nd(Bip)(Ur)_2]^{3+}$ and

TABLE-1
POLAROGRAPHIC CHARACTERISTICS AND $F_{ij}[x]$ FUNCTION OF Nd(III)-BIPYRIDYL-UREA TERNARY SYSTEM
Nd(III) = 1 mmol dm^{-3}, μ = 1.0, pH = 2.40 ± 0.02, urea = 0.1 mole dm^{-3}

S. No.	Conc. of bipyridyl mol dm^{-3}	$-E_{1/2}$ V *vs.* SCE	i_d (div)	$F_{00}(x) \times 10^{-2}$	$F_{10}(x) \times 10^{-4}$	$F_{20}(x) \times 10^{-5}$	$F_{30}(x) \times 10^{-7}$
1.	0.00	1.742	80	–	–	–	–
2.	0.02	1.754	75	8.54	1.62	2.65	1.27
3.	0.04	1.768	71	20.12	8.10	8.40	1.52
4.	0.06	1.774	65	48.10	7.98	10.32	1.60
5.	0.08	1.780	60	92.10	10.21	11.81	1.73
6.	0.10	1.796	58	152.78	15.10	19.50	1.78

A = 80, B = 1.0×10^4, C = 2.1×10^5, D = 1.1×10^7.

$[Nd(Bip)_2(Ur)]^{3+}$ have been found with their stability constants 4.90, 5.26 and 6.07 respectively. The calculated values of log K_m and log K_s are 1.02 and 0.72 respectively. These positive values reveal that mixed complexes are more stable than binary complexes. The tendency of ligand to add and substitute is shown in Scheme-1.



Scheme-I: Complex Equilibria in Nd(III)-Bipyridyl-Urea Ternary System

TABLE-2
POLAROGRAPHIC CHARACTERISTICS AND $F_{ij}[x]$ FUNCTION OF Nd(III)-BIPYRIDYL-UREA TERNARY SYSTEM
Nd(III) = 1 mmol dm^{-3}, μ = 1.0, pH = 2.40 ± 0.02, urea = 0.2 mol dm^{-3}

S. No.	Conc. of bipyridyl mol dm^{-3}	$-E_{1/2}$ V *vs.* SCE	i_d (div)	$F_{00}(x) \times 10^{-2}$	$F_{10}(x) \times 10^{-4}$	$F_{20}(x) \times 10^{-5}$	$F_{30}(x) \times 10^{-7}$
1.	0.00	1.742	80	–	–	–	–
2.	0.02	1.760	72	18.0	4.5	1.3	–
3.	0.04	1.781	67	44.3	9.2	1.8	1.9
4.	0.06	1.802	62	109.5	16.0	2.7	2.2
5.	0.08	1.812	58	280.0	32.8	3.9	3.6
6.	0.01	1.820	55	494.5	48.0	4.8	3.7

A = 700, B = 20×10^4, C = 1.0×10^5, D = 1.5×10^7.

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(*Received:* 16 August 2001; *Accepted:* 23 November 2001) AJC-2533