Asian Journal of Chemistry Vol. 14, No. 1 (2002), 349–356

Updated Spectrophotometric Investigation of Neodymium Complexes Formed with 1-(2-Pyridylazo)-2-Naphthal and 2-(5-Bromo-2-Pyridylazo)-5-Diethylamino-*m*-Phenol

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The updated investigation of neodymium complexes formed with two ligands: 1-(2-pyridylazo)-2-naphthal (PAN) (at pH 10) and 2-(5-bromo-2-pyridylazo)-5-diethylamino-m-phenol (5-Br-PADAP) (at pH 8) was made in detail by β-correction spectrophotometry. The nonionic surfactant, emulsifier OP was found to increase the sensitivity and solubility of ligand and complex. The characteristic factors were calculated, for example, complex ratio and stability constant. The results showed that $Nd(PAN)_2$ and $Nd(5\text{-Br-PADAP})_2$ were formed in this study and their real but not apparent molar absorptivities were the first to be determined as follows: $\varepsilon^{550}_{Nd(PAN)_2} = 4.54 \times 10^4$ at pH 10 and $\varepsilon^{560}_{Nd(5\text{-Br-PADAP})_2} = 8.4 \times 10^4$ L mol^{-1} cm^{-1}at pH 8. In addition, the cumulative stability constants of two complexes $Nd(PAN)_2$ and $Nd(5\text{-Br-PADAP})_2$ were still computed to be 1.04×10^{10} and 4.73×10^9 both in ionic strength 0.1 and at temperature 20°C respectively

Key words: β-correction principle, spectrophotometry, neodymium complex, PAN, 5-Br-PADAP.

Neodymium(Nd) is one of the lanthanides often exists in mengite and bastnasite. It has seven isotopes, all being stable. Because of the similar chemical properties, the mixture of rare earth elements is usually studied but the spectrophotometric investigation[1–3] of Nd complex is much less than rare earth elements complex. The latter was reported with ligands, for example azo compounds[4–6], acidic and basic dyes[7,8] and others[9,10]. Two ligands,1-(2-pyridylazo)-2-naphthal (PAN) and 2-(5-bromo-2-pyridylazo)-5-diethylamino-m-phenol (5-Br-PADAP) are the conventional indicators for complexing other metals, for example cobalt[11], silver[12] and iron[13]. In this report, the updated investigation of two Nd complexes with PAN and 5-Br-PADAP has been made by β-correction spectrophotometry[14] which may eliminate the interference of the excess ligand on absorbance of Nd complex. Such two ligands were ever used

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for the determination[15, 16] of rare earth elements by ordinary spectrophotometry in the past. However, it was found that Nd(III) is more sensitive to complex PAN at pH 10 and 5-Br-PADAP at pH 8 both in the presence of emulsifier OP than other rare earth elements. The β-correction spectrophotometric results showed that the formed complexes are expressed by $Nd(PAN)_2$ and $Nd(5\text{-Br-PADAP})_2$ and their real absorptivities were equal to $\varepsilon^{550}_{Nd(PAN)_2} = 4.54 \times 10^4$ and $\varepsilon^{560}_{Nd(5-Br-PADAP)_2} = 8.38 \times 10^5$ L mol^{-1} cm^{-1}. In addition, the β-correction method was still applied for the determination of the complex's step and cumulative stability constant. The operation is simpler and the result is more acceptable than other conventional methods, such as molar ratio[17], continuous variation[18], equilibrium movement[19] and Yatzimirsky[20] because it gave out the accurate absorption of Nd complex product in the mixed solution. On the contrary, the above conventional methods are often limited because of the effect of the excess of ligand.

Principle

From the following expression[14], the real absorbance (A_c) of a metal (M) complex (ML_γ) produced with a ligand (L) in solution is calculated:

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha\beta}$$

where ΔA and $\Delta A'$ are the absorbances of the mixed solution of ML_γ and L measured at wavelengths λ_2 and λ_1 against the reagent blank (only L solution), respectively and both α and β are named correction factors which are calculated as follows:

$$\alpha = \frac{\varepsilon^{\lambda_1}_{ML_\gamma}}{\varepsilon^{\lambda_2}_{ML_\gamma}} \quad \text{and} \quad \beta = \frac{\varepsilon^{\lambda_2}_{L}}{\varepsilon^{\lambda_1}_{L}}$$

where $\varepsilon^{\lambda_1}_{ML_\gamma}$, $\varepsilon^{\lambda_2}_{ML_\gamma}$, $\varepsilon^{\lambda_1}_{L}$ and $\varepsilon^{\lambda_2}_{L}$ are the molar absorptivities of ML_γ and L at wavelengths λ_1 and λ_2, respectively, whose ratio may be computed after the direct determination of L and ML_γ solutions.

The real but not apparent molar absorptivity ($\varepsilon^{\lambda_2}_{ML_\gamma}$) and the molar ratio (γ′) of the effective L to M may be expressed as follows:

$$\varepsilon^{\lambda_2}_{ML_\gamma} = \frac{A_c}{\delta C_M} \quad \text{and} \quad \eta = \frac{A_c - \Delta A}{A_0}$$

$$\gamma' = \eta \times \frac{C_L}{C_M}$$

where the symbol η is the effective part of ligand and both C_M and C_L are the molar concentrations (mol/L) of M and L in the beginning solution. The symbol δ is the thickness of cell used and A_0 is the absorbance of L solution measured at wavelength λ_2 against water reference. While γ′ reaches maximum we think

that $\gamma = \gamma'$, where γ is a natural number to be named the complex number or stoichiometric ratio of the complex produced. In addition, the following expression was the first to be established for determination of the nth stage ($0 < n < \gamma$) stability constant (K_n) of complex ML_γ from the reaction equation: $ML_{n-1} + L = ML_n$, which must use such a M-L solution to form the complex ratio γ' between $(n-1)$ and n.

$$K_n = \frac{\gamma' + 1 - n}{(n - \gamma')(C_L - \gamma' C_M)}$$

From each K_n we can further calculate the cumulative constant (K) of complex ML_γ from the following expression:

$$K = K_1 \times K_2 \times \ldots \times K_n \times \ldots \times K_\gamma$$

RESULTS AND DISCUSSION

Absorption spectra: The reactions between neodymium and PAN at pH 10 and 5-Br-PADAP at pH 8 are measured. By comparing curve 2-4 with curve 2-3, we found that the spectra of Nd-5-Br-PADAP complex solution in the presence of OP gives higher absorption than that in the absence of surfactant OP. By comparing curve 1-4 with 1-3, the absorption spectrum of the Nd-PAN complex solution may give higher sensitivity at pH 10 than that in KOH solution. From curves 1-3 and 2-3, the peak and valley absorptions locate at wavelengths $\lambda_1 = 470$ and $\lambda_2 = 550$ nm for the Nd-PAN reaction and 1-3 and $\lambda_1 = 450$ and $\lambda_2 = 560$ nm for the Nd-5-Br-PADAP reaction. We calculate β from curves 1-1 and 2-1

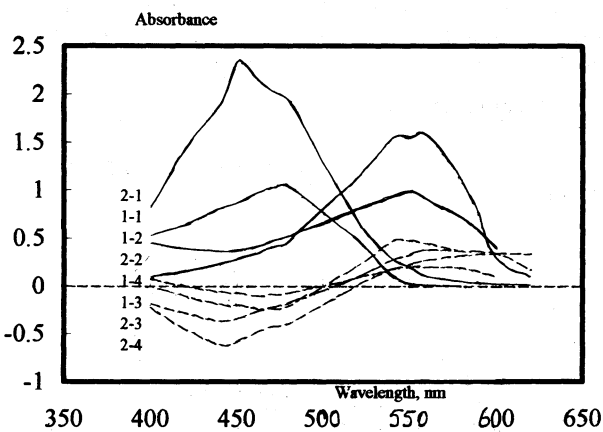

Fig. 1. Absorption spectra of reagent blank and neodymium complex solutions in the presence of OP: 1-, Nd-PAN complex reaction at pH 10; 2-, Nd-5-Br-PADAP complex reaction at pH 8. -1, reagent blank (in the absence of Nd but in the presence of 0.1% EDTA) against water; -2, only Nd-ligand complex (Nd much more than ligand concentration) against water; -3, Nd(1.60 mg/L for PAN and 0.80 mg/L for 5-Br-PADAP)-ligand solution against reagent blank 1-4, 1 mL of 5% KOH instead of pH 10 buffer solution; 2-4 in the absence of surfactant.

and α from curves 1-2 and 2-2. Therefore, the following equations are given: $A_c = 1.01(\Delta A - 0.029\Delta A')$ for Nd-PAN-OP complex at pH 10 and $A_c = 1.01(\Delta A - 0.048\Delta A')$ for Nd-5-Br-PADAP complex at pH 8.

Effect of ligand concentration: According to procedure, varied the addition of PAN and 5-Br-PADAP solution and the absorbances of neodymium complexes are shown in Fig. 2. We found that both the positive and negative absorptions approach maximum from curves 1-1 and 2-1 when the addition of PAN and 5-Br-PADAP solutions are over 1.5 mL. In addition, from curves 1-1 and 2-1, it was difficult for the complex ratio to be compared by molar ratio method[17]

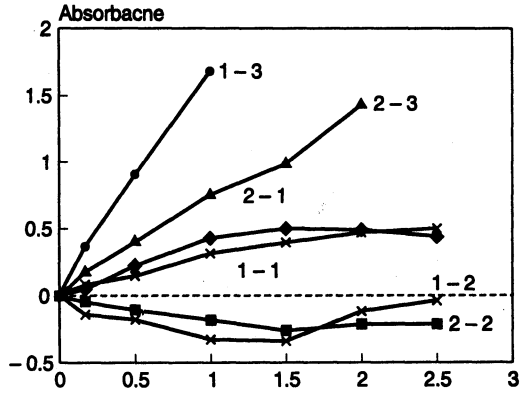

Fig. 2. Effect of ligand concentration on the measured absorbances in the presence of 0.2% OP: 1-, Nd-PAN complex reaction at pH 10; 2-, Nd-5-Br-PADAP complex reaction at pH 8. -1, Nd(1.60 mg/L for PAN and 0.80 mg/L for 5-Br-PADAP)-ligand solution against reagent blank at 550 (use of PAN) and 560 nm (use of 5-Br-PADAP); -2, same as -1 but at 470 (use of PAN) and 450 nm (use of 5-Br-PADAP); -3, reagent blank at 470 (use of PAN) and 450 nm (use of 5-Br-PADAP) against water

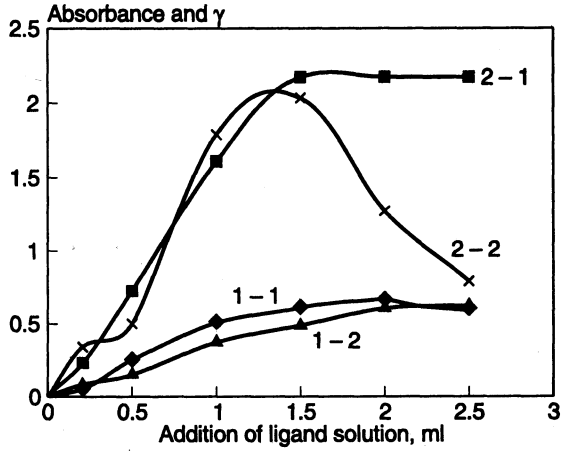

Fig. 3. Effect of ligand concentration on real absorbance A_c and the complex ratio, γ': 1-, Nd(1.60 mg/L)-PAN-OP complex reaction at pH 10; 2-, Nd(0.80 mg/L)-5-Br-PADAP-OP complex reaction at pH 8. -1, A_c at 550 (use of PAN) and 560 nm (use of 5-Br-PADAP); -2, γ'

because of the unclear inflexion point. Frorn curves in Fig. 2, the real absorbance (A_c) and complex ratio (γ) of each of the neodymium complexes can be calculated. They are shown in Fig. 3. From the maximal A_c of each curve, their real molar absorptivity is calculated as follows: $\varepsilon^{550}_{Nd(PAN)_2} = 4.54 \times 10^4$ at pH 10 and $\varepsilon^{560}_{Nd(5-Br-PADAP)_2} = 8.34 \times 10^4$ L mol–1 cm–1 at pH 8. From curves 1-1 and 2-1, both γ's of complexes approach to constant 2. Therefore, the complexes were formed as $Nd(PAN)_2$ and $Nd(5\text{-}Br\text{-}PADAP)_2$.

Effect of pH: By varying the pH of two solutions, the measurement of each was carried out. The absorbance changes are shown in Fig. 4. From curves x-1 and x-2, the complex of Nd-PAN-OP approaches to the maximal absorption at pH 10 and that of Nd-5-Br-PADAP at pH 8.

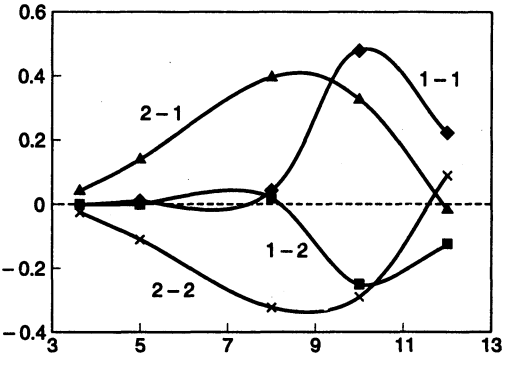

Fig. 4. Effect of pH on measurement of neodymium complex solution: 1-, Nd(1.60 mg/L)-PAN complex reaction at pH 10 ; 2-, Nd(0.80 mg/L)-5-Br-PADAP complex reaction at pH 8. -1, against reagent blank at 550 (use of PAN) and 560 nm (use of 5-Br-PADAP); -2, same as -1 but at 470 (use of PAN) and 450 nm (use of 5-Br-PADAP)

Effect of surfactant selection and addition: The effect of various surfactants is shown in Fig. 5. From curves x-1 and x-2, the non-ionic surfactant OP gives the maximal absorbance, which is over double that in the absence of surfactant. By varying the addition of 5% OP, the experimental result is shown in Fig. 6. From curves x-1 and x-2, both the complexes approach to maximal absorption when OP concentration is over 0.1%.

Effect of colour-developed time: The effects of time on the positive and negative absorbances are shown in Fig. 7. The absorbances reach maximum from curve 1-2 at the time over 10 min and from curve 2-2 at the time between 10 and 30 min.

Determination of stability constant: The following solutions were measured for the determination of stability constant of complexes: 0.278 μmol/25mL Nd(III) with 0.50, 1.00 μmol/25 mL PAN and 0.139 μmol/25 mL Nd(III) with 0.50 and 1.00 μmol/25 mL 5-Br-PADAP. The stepwise and cumulative stability constants are calculated and listed in Table-1.

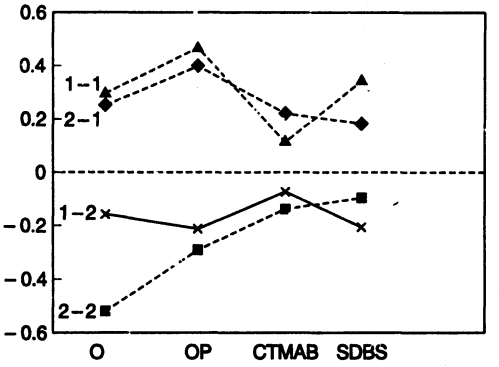

Fig. 5. Effect of various surfactants: 1-, Nd(1.60 mg/L)-PAN complex reaction at pH 10; 2-, Nd(0.80 mg/L)-5-Br-PADAP complex reaction at pH 8. -1, against reagent blank at 550 (use of PAN) and 560 nm (use of 5-Br-PADAP); -2, same as -1 but at 470 (use of PAN) and 450 nm (use of 5-Br-PADAP)

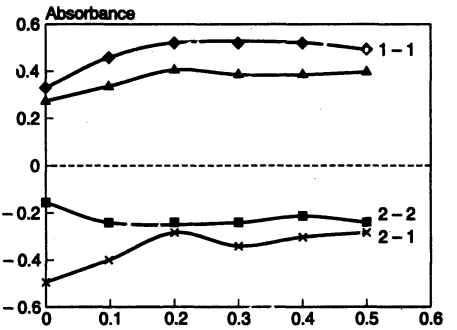

Fig. 6. Effect of the OP addition on the absorbance of neodymium complex solution: 1-, Nd(1.60 mg/L)-PAN complex reaction at pH 10 ; 2-, Nd(0.80 mg/L)-5-Br-PADAP complex reaction at pH 8. -1, against reagent blank at 550 (use of PAN) and 560 nm (use of 5-Br-PADAP); -2, same as -1 but at 470 (use of PAN) and 450 nm (use of 5-Br-PADAP).

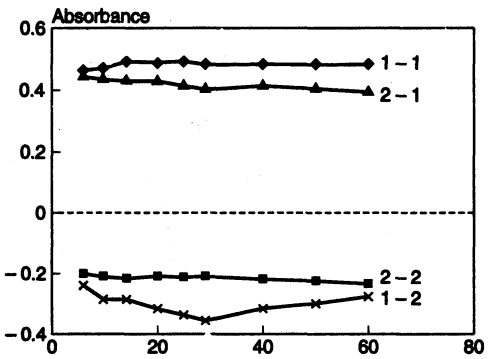

Fig. 7. Effect of the colour-developed time on measurement of neodymium complex solution: 1-, Nd(1.60 mg/L)-PAN complex reaction at pH 10; 2-, Nd(0.80 mg/L)-5-Br-PADAP complex reaction at pH 8. -1, against reagent blank at 550 (use of PAN) and 560 nm (use of 5-Br-PADAP); -2, same as -1 but at 470 (use of PAN) and 450 nm (use of 5-Br-PADAP)

TABLE-1
DETERMINATION OF STABILITY CONSTANT OF $Nd(PAN)_2$ AT pH 10 AND $Nd(5\text{-}Br\text{-}PADAP)_2$ AT pH 8 IN IONIC STRENGTH 0.1 M AT 20°C

Reaction	Absorbance		γ′	K
	ΔA′	ΔA		
Nd(0.278 μmol/25mL)-PAN(0.50 μmol/25mL)	–0.061	0.173	0.705	$K_1 = 1.96 \times 10^5$
	–0.058	0.169	0.681	$K_1 = 1.72 \times 10^5$
-PAN(1.00 μmol/25mL)	–0.131	0.429	1.590	$K_2 = 6.44 \times 10^4$
	–0.126	0.415	1.530	$K_2 = 4.90 \times 10^4$
				$K = 1.04 \times 10^{10}$
Nd(0.139 μmol/25mL)-5-Br-PADAP(0.50 μmol/25mL)	–0.096	0.109	0.513	$K_1 = 6.14 \times 10^4$
	–0.093	0.110	0.501	$K_1 = 5.83 \times 10^4$
	–0.293	0.340	1.730	$K_2 = 8.90 \times 10^4$
-5-Br-PADAP (1.00 μmol/25mL)	–0.285	0.334	1.680	$K_2 = 6.93 \times 10^4$
				$K = 4.73 \times 10^9$

EXPERIMENTAL

Absorbances were measured on a Lambert Recording Spectrophotometer (P.-E. Co.) with 1.0 cm cells.

Solutions and Reagents: PAN solution and 5-Br-PADAP solution, both 1.00 mmol/L, were prepared by dissolving 0.2493 g of 1-(2-pyridylazo)-2-naphthal (PAN, Shanghai Reagent) and 0.3490 g of 2-(5-bromo-2-pyridylazo)-5-diethyl-amino-*m*-phenol (5-Br-PADAP, Tianjin Reagent) in 1000 mL of acetone (Shanghai Reagent) and stored in dark bottles at *ca.* 5°C. Neodymium standard, 500 mg/L, was prepared by dissolving 0.857 g of neodymium sesquioxide (AR, Shanghai Reagent) in 10 mL of concentrated chlorhydric acid and diluted to 1000 ml with distilled water. 10.0 mg/L Nd use solution was prepared daily. The buffer solutions, pH 8 and pH 10 were prepared with ammonia water (AR, Beijing Chemical) and ammonium chloride (AR, Shanghai Chemical). The anion surfactant, sodium dodecyl benzene sulfonate (SDBS, Shanghai Reagent), nonionic surfactant, OP (Beijing Chemical) and cationic surfactant, cetyl trimethyl ammonium bromide (CTMAB, Shanghai Reagent) solutions all 5% were prepared for increasing the solubility of complex and ligand and sensitivity of complex.

Recommended Procedure: For Nd-PAN complex reaction: 40 μg neodymium was taken in a 25-mL calibrated flask. Added 2 mL of pH 10 buffer solution and 1 mL of 5% OP. Then varied the addition of 1.00 mmol/L PAN and diluted to the mark with water and mixed well. After 10 min, the absorbances were measured at two wavelengths 470 and 550 nm in 1.0-cm cell, respectively.

For Nd-5-Br-PADAP complex reaction: 20 μg neodymium was taken in a 25-mL calibrated flask. Added 2 mL of pH 8 buffer solution and 1 mL of 5% OP. Changed the addition of 1.00 mmol/L 5-Br-PADAP and diluted to the mark with water and mixed well. Between 10 and 30 min, the absorbances were measured at two wavelengths 450 and 560 nm in 1.0-cm cell, respectively.

ACKNOWLEDGEMENTS

This work was supported by both the Natural Science Foundation of Anhui Province (No. 99045332) and the '99 Climbing Program of China (Special).

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(*Received*: 29 August 2001; *Accepted*: 24 October 2001) AJC-2501