

Research Article

Calculating the Equilibrium Constants for All Monoazide Lanthanide Complexes in Aqueous Solution Based on the Formation of Eu(III)/N₃⁻

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Abstract Interest in lanthanide (Ln)/azide (N₃⁻) chemical interactions, especially those involving Eu(III), has recently increased because N₃⁻ quenches the luminescence of some lanthanides. Consequently, accurate equilibrium constant values for Ln/N₃⁻ complexes are useful thermodynamic data. Herein, potentiometrically determined equilibrium constant data for the Eu(N₃)₃²⁺ complex in aqueous solution at constant ionic strength (2.0 mol L⁻¹, with NaClO₄) and temperature (25.0 ± 0.1 °C) are reported. Data for the average number of ligands (\bar{n}) were obtained by measuring the pH of the Eu(III)/N₃⁻/HN₃ system. The relationship between the integrated \bar{n} versus [N₃⁻] curve, built by consecutively incrementing [N₃⁻], provided the Fronaeus function, F₀(L). This relationship (in the 0.010–0.10 mol L⁻¹ [N₃⁻] range) at four different Eu(III) concentrations (28.6–45.2 mmol L⁻¹) revealed a single mononuclear complex ($\beta_1 = 4.51 \text{ mol}^{-1} \text{ L}$). This β_1 value was used in a mathematical approach to calculate the β_1 values of all other lanthanides.

Keywords europium; azide; complex formation; stability constants; lanthanides

1. Introduction

Studies into lanthanide (Ln) azides have their origins in the last years of the nineteenth century. In 1896, Dennis was the first researcher to mention interactions between inorganic azides and lanthanides, describing the use of potassium azide (KN₃) as a precipitating agent for the quantitative separation of Th(IV) from other rare earths present in monazite, a mineral found in Brazil [1]. In 1931, Ant-Wuorinen used a sodium azide (NaN₃) solution to fractionally precipitate rare earths [2], and ten years later he separated rare earth alkalis by the electrolysis of their respective azides [3]. La(III) and Ce(III) were the first lanthanides to be evaluated separately in aqueous solution, and equilibrium constants of their complexes with N₃⁻ were determined by potentiometry [4]. Soon after, equilibrium constants for complexes formed between N₃⁻ and other Ln(III) ions in aqueous solution were determined. In 1975, Ezaby and Abdel-Aziz were

the first to publish spectrophotometrically determined data for the azide complexes of Pr(III), Nd(III), and Sm(III) [5].

In 1977, Cuillerdier et al. determined values for Nd(III) and Er(III) complexes by spectrophotometric and potentiometric methods [6]. In the same year, Godinho et al. determined equilibrium constants for the monoazide complexes of La(III), Nd(III), and Er(III) by spectrophotometry, and reported values that were of the same order of magnitude [7]. A decade later, Choppin and Barber studied the complexations of N₃⁻ with lanthanide (Ln³⁺) and actinide (An³⁺) ions using solvent extraction and radioanalysis, and showed that Ln³⁺ monoazide complexes, particularly those of Pm(III), Eu(III), and Tm(III), are slightly less stable than the An³⁺ monoazide complexes of Am(III), Cm(III), and Cf(III) [8].

Musikas et al. evaluated the formation of some Ln/N₃⁻ complexes by solvent extraction with thenoyltrifluoroacetone and spectroscopic techniques (specifically UV, Raman, and NMR), and reported that monoazide complexes of Nd(III), Eu(III), and Yb(III) have the same equilibrium constant values. They also mentioned the formation of azido complexes containing higher numbers of N₃⁻ groups for the same lanthanides, namely, Nd(III), Eu(III), and Yb(III), and two actinides, namely, Am(III) and Cm(III), in highly concentrated N₃⁻ solutions [9].

Despite the above-mentioned studies, interactions between N₃⁻ and all 4f block elements in an aqueous solution have not been extensively studied to date. The currently available data are also not completely conclusive, which is ascribable to the high oxophilicity of lanthanides, resulting in an unfavourable competition between the azide ion and water, with Ln(III) ions preferring oxygen donor ligands; hence, methods using different analytical techniques are required for determining these equilibrium constant values.

Interest in chemical interactions between N_3^- and Ln(III) ions, especially Eu(III), has increased over the past few decades because N_3^- is able to quench the luminescence of some Ln(III) ions in aqueous [10,11] and nonaqueous [12] solutions. Therefore, the value of the equilibrium constant of the complex formed between Eu(III) and N_3^- obtained under careful experimental conditions and high precision is very useful thermodynamic information.

In the present study, we carefully determined the value of the formation constant, β_1 , for the $\text{Eu}(\text{N}_3)^{2+}$ monoazide complex in aqueous solution using a calibrated glass electrode, constant ionic strength, and temperature control. In addition, this β_1 value was then used in a mathematical procedure to calculate the equilibrium constants of the monoazide complexes of all other 4f block elements. This approach provides a reasonable alternative method for determining values that have not yet been obtained experimentally.

2. Experimental

2.1. Materials

A Metrohm 654 pH meter and glass electrode (Metrohm AG, Herisau) combined with a Ag/AgCl reference electrode (6.0210.100) filled with 3.0 mol L^{-1} NaCl, was used at $25.0 \pm 0.1^\circ \text{C}$ in the pH experiments in this study.

2.2. Chemicals

All reagents were of analytical-grade and were obtained from Merck, Sigma-Aldrich or Fluka Chemie A. G. Deionised water was used to prepare all solutions.

A 5.48 mol L^{-1} sodium perchlorate (NaClO_4 , $122.44 \text{ g mol}^{-1}$, Merck) solution was prepared by dissolving of 671.0 g of NaClO_4 in 1.0 L of water in a volumetric flask. The solution was standardised by gravimetry by taking small aliquots (2.00 – 3.50 mL) and drying in an oven at 120°C to constant weight [13,14,15].

A 1.0 mol L^{-1} sodium hydroxide (NaOH , 40.00 g mol^{-1} , Merck) solution and a 0.250 mol L^{-1} sulfuric acid (H_2SO_4 , 98.08 g mol^{-1} , Merck) solution were prepared and standardised as described elsewhere [16].

A 1.0 mol L^{-1} perchloric acid solution was prepared by dissolving HClO_4 ($100.46 \text{ g mol}^{-1}$, $d = 1.67 \text{ g mL}^{-1}$, 70–72%, Merck) in water and standardising with a 1.0 mol L^{-1} NaOH solution.

A 4.38 mol L^{-1} sodium azide (NaN_3 , 65.01 g mol^{-1} , Merck) solution was prepared by dissolving 284.7 g of NaN_3 in 1.0 L of water in a volumetric flask. Standardisation was achieved by adding 25.0 mL of a 0.250 mol L^{-1} H_2SO_4 solution in 2.0 mL of 4.38 mol L^{-1} NaN_3 solution, boiling to remove the volatile hydrazoic acid (HN_3), followed by back titration of the remaining H_2SO_4 solution with a 1.0 mol L^{-1} NaOH solution and phenolphthalein as indicator [13,14,15].

A 0.35 mol L^{-1} Eu(III) perchlorate ($\text{Eu}(\text{ClO}_4)_3$) solution was prepared by directly reacting Eu(III) oxide (Eu_2O_3 , $351.93 \text{ g mol}^{-1}$, 99.9%, Sigma-Aldrich) with HClO_4 . Eu_2O_3 ($\sim 3.5 \text{ g}$) was transferred to a 1.0 L beaker containing 500 mL water and then perchloric acid (HClO_4 , $100.46 \text{ g mol}^{-1}$, $d = 1.67 \text{ g mL}^{-1}$, 70–72%, Merck) was slowly added in excess [17]. Mild heating was required to dissolve the Eu_2O_3 . After filtering off the excess unreacted Eu_2O_3 , the obtained solution was 10-fold concentrated by controlled evaporation ($\sim 50 \text{ mL}$), after which a 1.0 mol L^{-1} HClO_4 solution was used to adjust the pH to 2.0 in order to prevent hydrolysis [18]. Standardisation was carried out by complexometric titration with EDTA [19]. Briefly, 1.00 mL of the $\text{Eu}(\text{ClO}_4)_3$ solution was transferred to a 25-mL conical flask and hexamethylenetetramine powder was added until pH 6.0 was achieved, after which 100 mg of a xylene orange: KNO_3 mixture (1:90 w/w) was added and the solution was titrated with a 0.01 mol L^{-1} EDTA solution until the colour changed from purplish red to yellow.

2.3. Working solutions and strategy

Ten different N_3^-/HN_3 buffer working solutions (10.0 mL) were prepared by mixing (115 – $1.140 \mu\text{L}$) of 4.38 mol L^{-1} NaN_3 with (250 – $2.490 \mu\text{L}$) of 1.0 mol L^{-1} HClO_4 . The N_3^- concentrations in these working solutions ranged between 0.010 mol L^{-1} and 0.10 mol L^{-1} . The ionic strength was adjusted to 2.0 mol L^{-1} by adding (9.0 – 8.2 mL) of 5.48 mol L^{-1} NaClO_4 .

Four amounts (0.900 – $1.500 \mu\text{L}$) of $0.3482 \text{ mol L}^{-1}$ $\text{Eu}(\text{ClO}_4)_3$ solution were added to separate samples of each N_3^-/HN_3 buffer working solution such that the Eu(III) concentrations in the final solutions ranged from 28.6 mmol L^{-1} to 45.2 mmol L^{-1} . Changes in pH were measured from the initial (pH_1) to the final (pH_2) value after adding the Eu(III) solution to the N_3^-/HN_3 buffers, and followed potentiometrically using a calibrated glass electrode.

2.4. Potentiometric measurements and data treatment

In order to measure the hydrogen ion concentration, a 0.05 mol L^{-1} potassium phthalate buffer solution (conditional $\text{pH} = 3.812$) with the same ionic strength as the working solutions (2.00 mol L^{-1} , NaClO_4) was used to calibrate the glass electrode [13,14,15]. This potassium phthalate solution had been previously calibrated with a $0.0100 \text{ mol L}^{-1}$ HClO_4 solution at the same ionic strength (2.00 mol L^{-1} ; NaClO_4).

3. Results and discussion

The mass balances and the Henderson-Hasselbalch equation (1) for buffer solutions were applied to the N_3^-/HN_3 system in which N_3^- acts as both a ligand for Eu(III) and as a component of the buffer solution [13,14,15,20].

Table 1: Calculated values of the Fronaeus function, $F_0(L)$, determined by integrating the \bar{n} versus $[N_3^-]_2$ data ($I = 2.00 \text{ mol L}^{-1}$ (NaClO_4); $T = 25.0 \pm 0.1 \text{ }^\circ\text{C}$).

pH ₁	pK HN ₃	$[N_3^-]_1 \times 10^{-2} (\text{mol L}^{-1})$	$C_{\text{Eu(III)}} \times 10^{-3} (\text{mol L}^{-1})$	pH ₂	$[N_3^-]_2 \times 10^{-3} (\text{mol L}^{-1})$	\bar{n}	$F_0(L)$
4.630	4.628	1.002	39.85	4.387	5.718	0.033	1.034
4.630	4.628	1.002	45.18	4.421	6.162	0.035	1.037
4.630	4.628	1.002	34.33	4.452	6.593	0.038	1.040
4.630	4.628	1.002	28.59	4.485	7.087	0.041	1.043
4.575	4.574	2.003	45.18	4.444	13.67	0.049	1.074
4.575	4.574	2.003	39.85	4.463	14.37	0.050	1.077
4.575	4.574	2.003	34.33	4.483	15.14	0.052	1.079
4.575	4.574	2.003	28.59	4.502	15.92	0.053	1.082
4.636	4.635	3.002	45.18	4.527	20.92	0.082	1.102
4.636	4.635	3.002	39.85	4.542	21.87	0.085	1.106
4.636	4.635	3.002	34.33	4.556	22.81	0.091	1.110
4.636	4.635	3.002	28.59	4.569	23.74	0.100	1.115
4.636	4.630	5.002	45.18	4.559	36.66	0.119	1.169
4.636	4.630	5.002	39.85	4.571	38.16	0.120	1.175
4.636	4.630	5.002	34.33	4.581	39.56	0.128	1.180
4.636	4.630	5.002	28.59	4.593	41.20	0.131	1.186
4.662	4.647	6.003	45.18	4.569	43.54	0.159	1.196
4.662	4.647	6.003	39.85	4.579	45.16	0.167	1.203
4.662	4.647	6.003	34.33	4.588	46.73	0.181	1.210
4.662	4.647	6.003	28.59	4.598	48.49	0.197	1.218
4.638	4.637	7.002	28.59	4.596	57.46	0.205	1.261
4.607	4.606	9.002	39.85	4.556	70.13	0.207	1.313
4.607	4.606	9.002	34.33	4.564	72.50	0.218	1.323
4.607	4.606	9.002	28.59	4.574	75.32	0.222	1.334
4.681	4.681	10.02	34.33	4.644	81.17	0.228	1.357
4.681	4.681	10.02	28.59	4.652	83.97	0.240	1.367

After reaching chemical equilibrium, the pH measurement provides the equilibrium concentrations, namely $[N_3^-]_1$ and $[HN_3]_1$. Subsequent addition of 0.35 mol L^{-1} $\text{Eu}(\text{ClO}_4)_3$ solution results in a new equilibrium condition for pH₂ and, consequently, values of $[N_3^-]_2$ and $[HN_3]_2$ [13, 14, 15]:

$$\text{pH} = \text{pK}_{\text{HN}_3} + \log \frac{[N_3^-]}{[HN_3]}. \quad (1)$$

A conditional pK_a for HN₃ at an ionic strength of 2.00 mol L^{-1} (NaClO_4) and a temperature (T) of $25.0 \pm 0.1 \text{ }^\circ\text{C}$ were determined for each pH experiment. Determining the pK_a values in different experiments has been found to be a reliable procedure as it corrects for any drift in junction potential, small losses of volatile HN₃, and even possible slope deviations of the glass electrode. The mean pK_a value for HN₃ was determined to be 4.626 ± 0.028 under these experimental conditions.

Because the formation and stability of the $\text{Eu(III)}/N_3^-$ complex is pH-dependent and hydrolytic species, such as $\text{Eu}(\text{OH})_2^+$, may be present in solutions at $\text{pH} > 6.0$ [21], the experimental approach used in the present potentiometric study is advantageous since the pH of the N_3^-/HN_3 buffer solution lies in the 4.4–4.7 range (Table 1) and such hydrolytic species are unlikely to be present.

The average number of ligands, \bar{n} (Bjerrum's function) [20, 22], was determined using QuickBasic 4.50 (Microsoft) (as described elsewhere [13]) by employing (2),

$$\bar{n} = \frac{(\text{CL} - [\text{L}])}{\text{CM}} = \frac{[\text{ML}] + 2 \cdot [\text{ML}_2] + \dots + n \cdot [\text{ML}_n]}{[\text{M}] + [\text{ML}] + [\text{ML}_2] + \dots + [\text{ML}_n]} \quad (2)$$

$$= \frac{\beta_1 \cdot [\text{L}] + 2 \cdot \beta_2 \cdot [\text{L}]^2 + \dots + n \cdot \beta_n \cdot [\text{L}]^n}{1 + \beta_1 \cdot [\text{L}] + \beta_2 \cdot [\text{L}]^2 + \dots + \beta_n \cdot [\text{L}]^n},$$

where CL, CM, [L], [M], [ML], and β are the analytical concentration of the ligand, the analytical concentration of the cation, the equilibrium concentration of the ligand, the equilibrium concentration of the cation, the equilibrium concentration of the complex, and the stability constant [22], respectively.

An \bar{n} versus $[N_3^-]_2$ curve was built by taking small and consecutive increments of $[N_3^-]_2$ [20, 22]. Since the same \bar{n} versus $[N_3^-]_2$ curve (Figure 1) was obtained at the four Eu(III) concentrations, $C_{\text{Eu(III)}}$, we concluded that no polynuclear complexes are formed in the Eu(III) concentration range used ($28.60\text{--}45.18 \text{ mmol L}^{-1}$) in this study.

A computer program elaborated in QuickBasic 4.50 (Microsoft) [13, 14, 15, 23] was used to integrate the \bar{n}

Table 2: Selected equilibrium constants, β_1 , for the monoazide complexes of lanthanides.

Ln	<i>a</i>	<i>b</i>	β_1 (mol ⁻¹ L)	I (mol L ⁻¹)	Method	Ref.
La(III)	(1.0000)	(0.000)	3.70	—	Mathematical	(c)
			4.20 ± 1.0	1.0	Spectrophotometry	7
			4.46 ± 1.02	3.0 (e)	Potentiometry	4
Ce(III)	1.0354	0.027	4.12	—	Mathematical	(c)
			4.36 ± 1.02	3.0 (e)	Potentiometry	4
Pr(III)	1.0639	0.051	4.52	—	Mathematical	(c)
			0.298 ± 0.03	2.0	Spectrophotometry (Scott method)	5
			0.246 ± 0.06	2.0	Spectrophotometry (dilution method)	5
Nd(III)	1.0869	0.053	4.68	—	Mathematical	(c)
			3.80 ± 1.0	1.0	Spectrophotometry	7
			0.501 ± 0.05	2.0	Spectrophotometry (Scott method)	5
			0.499 ± 0.02	2.0	Spectrophotometry (dilution method)	5
			2.5	NA	NMR, UV, and Raman	9
Pm(III)			3.31 ± 0.48	0.5 (e)	Radioanalysis	8
Sm(III)	1.1204	−0.007	4.26	—	Mathematical	(c)
			1.65 ± 0.04	2.0	Spectrophotometry (Scott method)	5
			1.69 ± 0.08	2.0	Spectrophotometry (dilution method)	5
Eu(III)			3.75 ± 0.33	0.5 (e)	Radio analysis	8
			2.5	NA	NMR, UV, and Raman	9
	1.1367	0.009	4.51 ± 0.11	2.0 (e)	Potentiometry	(d)
Gd(III)	1.1357	−0.143	3.18	—	Mathematical	(c)
Tb(III)	1.1693	−0.271	2.47	—	Mathematical	(d)
Dy(III)	1.1792	−0.366	2.01	—	Mathematical	(c)
Ho(III)	1.1796	−0.345	2.11	—	Mathematical	(c)
Er(III)	1.1900	−0.326	2.24	—	Mathematical	(c)
			3.90 ± 1.0	1.0	Spectrophotometry	7
			1.2	NA	NMR, UV, and Raman	9
Tm(III)	1.1833	−0.106	3.68	—	Mathematical	(c)
			3.21 ± 0.4	0.5 (e)	Radio analysis	8
Yb(III)	1.2023	−0.240	2.77	—	Mathematical	(c)
			2.5	NA	NMR, UV, and Raman	9
Lu(III)	1.2022	−0.053	4.26	—	Mathematical	(c)

All studies were performed at T = 25 °C [5,9] and there is no mention of temperature control; “*a*” and “*b*” are the parameters of (4) developed by Kumok and Serebrennikov [24]. “Mathematical” means obtained using (4) developed by Kumok and Serebrennikov [24]. (c) Calculated value in the present work using (4). (d) Present work. (e) NaClO₄ was used to maintain constant ionic strength. NA: not available.

versus $[\text{N}_3^-]_2$ curve to obtain the Fronaeus function, $F_0(L)$, as shown in (3) [20]:

$$F_0(L) = 1 + \sum_{n=1}^n [\text{N}_3^-]^n. \quad (3)$$

Treatment of the $F_0(L)$ data using a computer method for determining equilibrium constants [13,14,15] revealed solely the formation of the Eu(III) monoazide complex ($\text{Eu}(\text{N}_3)^{2+}$) under these experimental conditions, with a β_1 value of $4.51 \pm 0.11 \text{ mol}^{-1} \text{ L}$.

Table 2 lists a selection of literature-reported equilibrium constant data for monoazide lanthanide complexes, $\text{Ln}(\text{N}_3)^{2+}$. Most of these values were determined by spectrophotometry or potentiometry, which are very useful techniques for this purpose. Table 2 reveals that most equilibrium constants are of the same order of magnitude.

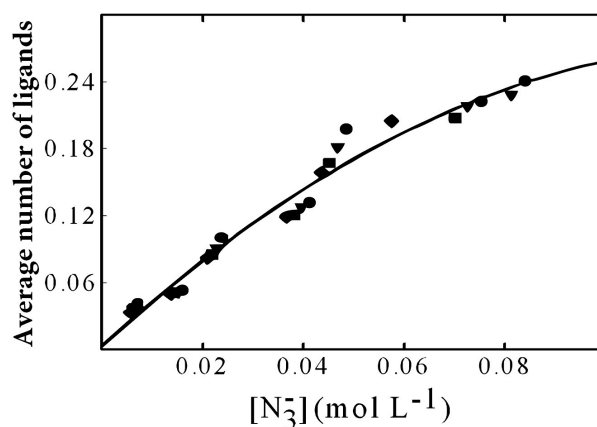


Figure 1: Curve describing the formation of the $\text{Eu(III)}/\text{N}_3^-$ system ($C_{\text{Eu(III)}}/\text{mol L}^{-1}$: $\bullet = 28.60 \times 10^{-3}$, $\blacktriangledown = 34.32 \times 10^{-3}$, $\blacksquare = 39.85 \times 10^{-3}$, and $\blacklozenge = 45.18 \times 10^{-3}$).

The equilibrium constants for Pr(III), Nd(III), and Sm(III) with N_3^- obtained using the Scott and dilution methods [5] are in good agreement; however, these low values do not agree with those obtained by other authors, and these differences cannot be attributed solely to the absence of temperature control in these experiments. In the study reported by El Ezaby and Abdel-Aziz [5], two absorbent species were found in solution; one was assumed to be Ln(III), with the other the corresponding azide complex. These two species were determined only by graphical methods, and the calculational methods (Scott's equation and dilution) were used with some modifications to suit conditions under which Ln(III) ions and their complexes absorb at the same wavelength, which may provide reasons for the low equilibrium constant values obtained.

Kumok and Serebrennikov [24] statistically evaluated the global equilibrium constants, β_1 , of rare-earth, except Pm(III), monocomplexes with 55 different ligands, and found that the logarithms of the β_1 values were linearly correlated. According to these authors, the β_1 value of any lanthanide monocomplex (LnL) is related to that of the lanthanum monocomplex (LaL) through (4). In this equation, a and b are constants obtained by statistically treating each trivalent Ln cation, and $\log \beta_{1(LnL)}$ and $\log \beta_{1(LaL)}$ refer to the monocomplexes of the lanthanide (Ln) and lanthanum (La), respectively,

$$\log \beta_{1(LnL)} = a \times \log \beta_{1(LaL)} + b. \quad (4)$$

The a and b values for Eu(III) are 1.1367 and 0.009, respectively [24]. With this in mind, we applied (4) to the β_1 value found in the present study for $Eu(N_3)^{2+}$ (i.e., $4.51 \text{ mol}^{-1} \text{ L}$), which provided $3.70 \text{ mol}^{-1} \text{ L}$ as the β_1 value for $La(N_3)^{2+}$. Since the values of a and b for trivalent Ln cations have been reported [24], the β_1 values were calculated for the monoazide complexes of all lanthanides, the results of which are listed in Table 2.

As expected, these complexes are very weakly bound since trivalent lanthanides are hard cations [25] and prefer to form complexes with oxygen or mixed oxygen-nitrogen donor ligands rather than nitrogen donors such as N_3^- . Despite being weak, the equilibrium constants calculated using only the equation developed by Kumok and Serebrennikov [24] for the Ln monocomplexes with N_3^- also need to be determined experimentally. The values obtained experimentally will facilitate a more realistic interpretation of the calculational methodology used in the present study for determining these same values mathematically.

4. Conclusions

Potentiometric measurements using a calibrated glass electrode at constant ionic strength (2.0 mol L^{-1} ; $NaClO_4$) and controlled temperature ($T = 25.0^\circ \text{C}$) enabled the accurate determination of the formation constant for the $Eu(N_3)^{2+}$

complex in aqueous solution ($\beta_1 = 4.51 \pm 0.11 \text{ mol}^{-1} \text{ L}$). No polynuclear complex is formed in the Eu(III) concentration range used in this study ($28.60\text{--}45.18 \text{ mmol L}^{-1}$). The β_1 value found for the $Eu(N_3)^{2+}$ complex was used in a mathematical approach to calculate the β_1 values for the monoazide complexes of all other 4f block elements, which provides a reasonable alternative procedure for determining values that have not yet been obtained experimentally.

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Conflict of interest The authors declare that they have no conflict of interest.

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