



METHODS TO DETERMINE THE STABILITY CONSTANT OF COMPLEX WITH A REFERENCE TO SPECTROPHOTOMETRY METHOD

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Abstract

The low water mole fraction stock solutions were made in methanol, and water is added later by volume into the working solutions. The water in the methanolic stock was removed at low pressure and 60°C several times using the Buchi 01 1 Rotavapor after first removing the methanol and the methanol-water mixture. Methanol was then added to the anhydrous mixture in order to make the methanolic stock.

Introduction

The water content was determined by Karl Fischer automatic titrations utilizing a Metrohm Automat E547 with an electronic buret. The sodium perchlorate stock solution was made by reacting sodium bicarbonate with concentrated perchloric acid :



Working solutions were prepared by diluting the stock in 10 ml volumetric flasks. A buret was used to add the stock solution into the flasks. Sodium nitrate was the source of the ligand and sodium perchlorate was required to maintain the ionic strength at 3.0. For the low water mole

fraction solutions, lithium nitrate (J. T. Baker Chemicals) and lithium perchlorate (Alfa Products, anhydrous 99.5 %) were used because they were more soluble than the sodium salts in this solvent. Even though Na^+ and Li^+ ions often cause different effects, the differences are negligible in this study because of the approximate similarity in the activity coefficient values. At an ionic strength of 0.1, the activity coefficient for Li^+ is 0.8 and for Na^+ it is 0.78. At higher ionic strength, the Ions (Li^+ and Na^+) lose some of their effectiveness and their activity coefficients decrease. Therefore, by maintaining a high ionic strength, the differences in the activity coefficients are kept at a minimum value. It is also essential to keep the Ionic strength constant, since at constant ionic strength the activity coefficients remain unchanged in the mass law equations.

A small computer program was written in BASIC in order to calculate the concentration of ClO_4^- required to keep the ionic strength at 3.0 for given concentrations of Nd^{3+} and NO_3^- ions. The formula for ionic strength is given by equation (13)

$$I = 1/2(m_1z_1^2+m_2z_2^2 + \dots) \quad (13)$$

where m_1, m_2, \dots represent the molar concentrations of the various ions in the solution and z_1, z_2 are their respective charges. Assuming that only the mono-complex forms,

$$I = 3.0 = 1/2 ([\text{Nd}^{3+}]3^2 + [\text{NdNO}_3^{2+}]2^2 + [\text{Na}^+] + [\text{ClO}_4^-] + [\text{NO}_3^-]) \dots \quad (14)$$

$$3 = 1/2 \{ (a-x)9 + 4x + (c+b) + (b+3a) + (c-x) \}$$

$$b = 3 + 3x + -6a - c \dots \quad (15)$$

where $a = [\text{Nd}(\text{ClO}_4)_3]$

$b = [\text{NaClO}_4]_3$

$c = [\text{NaNO}_3]$

$x = [\text{NdNO}_3^{2+}]$ (the amount of mono-complex formed) then the complex formation is given by

$$\text{Nd}^{3+} + \text{NO}_3^- = \text{NdNO}_3^{2+} \dots \quad (16)$$

The equilibrium constant is :

$$K_1 = \frac{[\text{NdNO}_3^{2+}]}{[\text{Nd}^{3+}][\text{NO}_3^-]} \dots\dots\dots (17)$$

which can be written as

$$K_1 = \frac{x}{(a-x)(c-x)} \dots\dots\dots (18)$$

in order to have a program that will calculate $[\text{Nd}(\text{C1O}_4)_3]$ and $[\text{NaNO}_3]$ as the inputs. For a 1:2 complex, several modifications were made :

$$\text{free } [\text{Nd}^{3+}] = z = a - x - y \dots\dots\dots (19)$$

$$\text{free } [\text{NO}_3^-] = d = c - x - 2y \dots\dots\dots (20)$$

(16) then becomes

$$K_1 = \frac{x}{(a-x-y)(c-x-2y)} * \frac{x}{[z][c]} \dots\dots\dots (21)$$

$$K_2 = \frac{[\text{Nd}(\text{NO}_3)_2^+]}{[\text{NdNO}_3^{2+}][\text{NO}_3^-]} \dots\dots\dots (22)$$

where $y = [\text{Nd}(\text{NO}_3)_2^+]$ (the amount of bis-complexes formed)

$$\text{thus, } K_2 = \frac{y}{(x)(c-x-2y)} = \frac{y}{[x][c]} \dots\dots\dots (23)$$

Rearranging (18) gives

$$a = z + x + y \dots\dots\dots (24)$$

Combining these equations gives :

$$a = z + K_1[z][c] + K_2[c][x]$$

$$a = z + K_1[z][c] + K_1K_2[z][c]^2$$

$$a = z(1 + K_1[c] + K_1K_2[C]^2)$$

Therefore:

$$z = \frac{a}{1 + K_1[c] + K_1K_2[c]^2} \dots\dots\dots (25)$$

In which:

$$x = K_1(c)(z) = [\text{NdNO}_3^{2+}] \dots\dots\dots (26)$$

$$y = K_1K_2(z)(c)^2 = [\text{Nd}(\text{NO}_3)_2^+] \dots\dots\dots (27)$$

The new ionic strength equation is :

$$2I = 9(\text{Nd}^{3+}) + 4(\text{NdNO}_3^{2+}) + [\text{Nd}(\text{NO}_3)_2^+] + [\text{L1}^+] + [\text{ClO}_4^-] + [\text{NO}_3^-]$$

$$6 = (9a - 9x - 9y) + 4x + y + c + b + (3a + b) + (c - x - 2y)$$

$$6 = 12a - 6x - 10y + 2c + 2b \quad 3 = 6a - 3x - 5y + c + b$$

$$b = 3 - 6a + 3x + 5y + c \dots\dots\dots(28)$$

where free $[\text{ClO}_4^-] = 3a + c$, since $[\text{Nd}(\text{ClO}_4)_3] = a$, $[\text{LINO}_3^-] = c$ and free $[\text{L1}^+] = c + b$, where b is the amount of $[\text{LClO}_4]$ that is needed.

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Absorbance measurements were made using the Gilford Model 2600 UV-VIS single beam spectrophotometer. The temperature was regulated using the Gilford Thermostat which measures and reproduces the temperature to within 0.1°C. The spectrometer was also interfaced to an Apple III computer; this allowed the storage of both the digital and the graphical output. The cell compartment of the spectrometer can hold up to four quartz cells, thus permitting one reference solution and three sample solutions to be measured at one run. The Gilford was programmed to function in the difference spectral mode; It subtracts the reference solution from each sample solution. The reference solution is either water, methanol, or water mixed with methanol; the choice is based on the solvent system being studied.

In order to choose the most sensitive wavelengths for making the absorbance measurements, a solution of $\text{Nd}(\text{NO}_3)_3$ at 0.3 M was made, and its absorbance minus the absorbance of 0.3 M solution of $\text{Nd}(\text{ClO}_4)_3$ was measured from 340 nm to 700 nm. From this difference spectrum of absorbance versus wavelength, four peaks with the highest maximum absorbances were chosen: 346.7 nm, 354.7 nm, 522.1 nm and 575.8 nm (Fig. 1).

Then, plots of the absorbance versus the ratio of the concentration of perchlorate ions to the constant Nd(III) ions concentration were made at the four wavelengths (Figs. 2 and 3). All the plots show horizontal straight lines, indicating that there is no change in the absorption due to the perchlorate ions. This probably indicates the absence of measurable complexation between the neodymium and the perchlorate ions, since in the analogous Er(III) ion

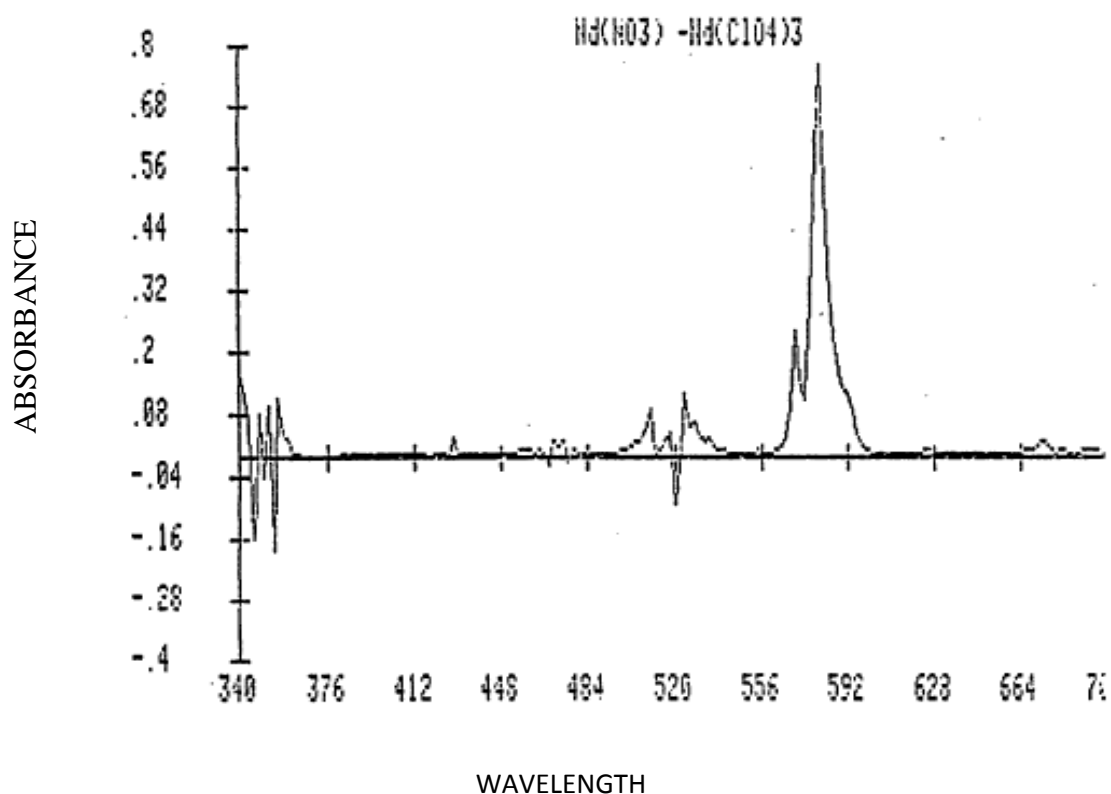


Figure 1. Difference spectrum of absorbance vs. wavelength.

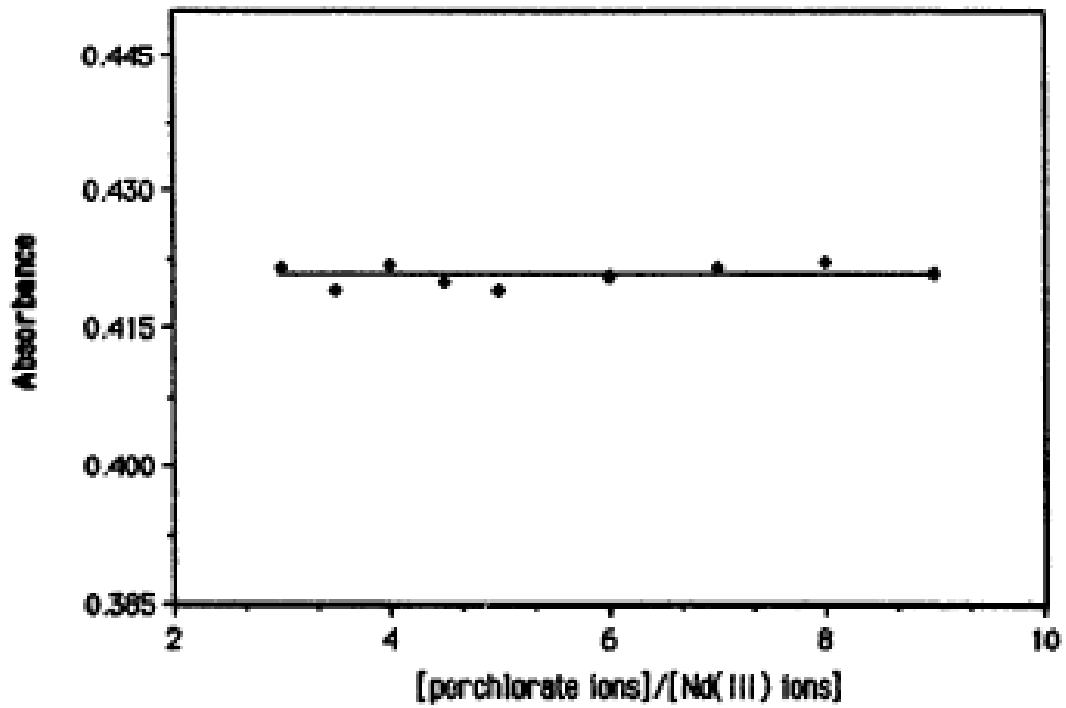


Figure 2: Absorbance vs. [perchlorate ions]/[neodymium (III) ions] at 521.7 nm

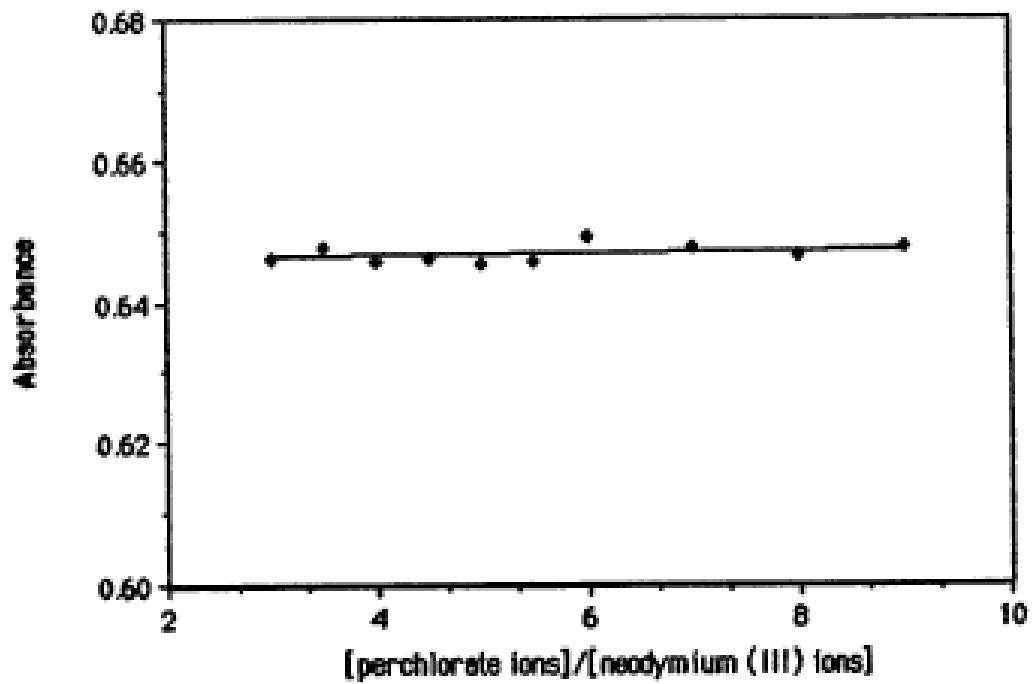


Figure 3: Absorbance vs. [perchlorate ions]/[neodymium (III) ions] at 575.3 nm

system, perchlorate Ion does change the absorption due to the formation of a complex. Further confirmation is obtained from Beer's Law plots of $\text{Nd}(\text{ClO}_4)_3$; all the plots obey Beer's Law.

Discussion

Several solutions of $\text{Nd}(\text{NO}_3)_3$ at various concentrations were then made and their absorbance were measured at these four wavelengths. Beer's Law plots were constructed at these four wavelengths; all four show deviations from the Beer's Law. In order to select the most sensitive wavelengths, absorbance measurements were made from 520.5 to 523.5 nm and from 573.5 to 583.5 nm. Two wavelengths with the highest absorption Intensity were selected (Figs. 6, 7). The wavelengths are 521.7 and 575.3 nm, and so absorbance data for the mole ratio plots were taken at these wavelengths, and also at four other wavelengths slightly higher and lower than the absorbance maxima. The six wavelengths are 521.2, 521.7, 522.2, 574.8, 575.3, and 575.8 nm.

The solutions for the measurements at the six wavelengths had the same concentration of neodymium perchlorate, varying concentration of the ligand (NO_3^-), and calculated concentration of the perchlorate ions (using the ionic strength program). Mole ratio plots, which are plots of the absorbance vs. $[\text{NO}_3^-]/[\text{Nd}(\text{III})]$, were then made in order to determine the number of complexes formed. The mole ratio plot (Fig. 8) shows the Intersection of two straight lines. The point of intersection indicates the number of complexes formed. This information together with the absorption data, guessed log of equilibrium constants ($\log \beta$'s), the ϵ_M 's (extinction coefficients of the metal), ϵ_{ML} 's (extinction coefficients of the complexes), and the ϵ_L 's (extinction coefficients of the ligands) were then entered into the Gaizer Multiple Wavelength Program.

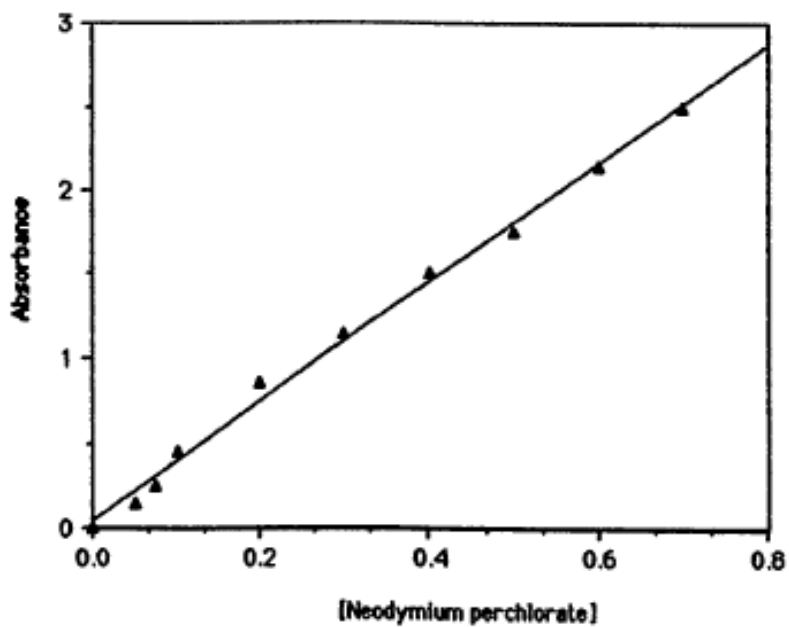


Figure 4. Beer's Law Plot for neodymium perchlorate at 521.7 nm

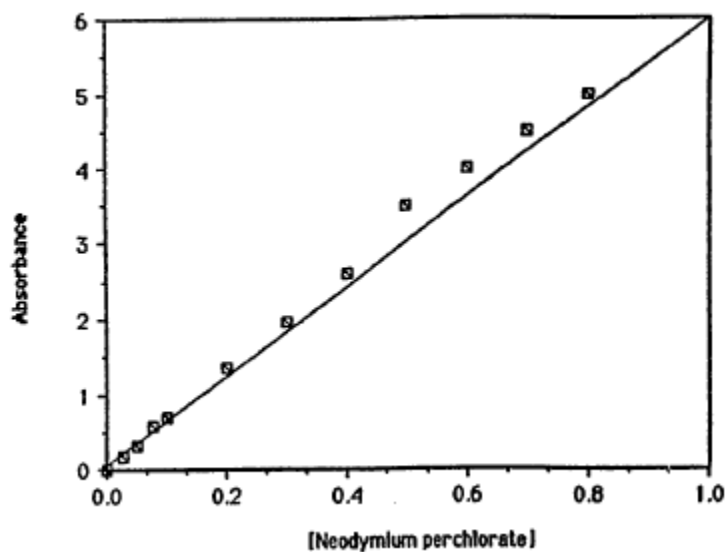


Figure 5. Beer's Law Plot of neodymium (III) nitrate at 575.3 nm

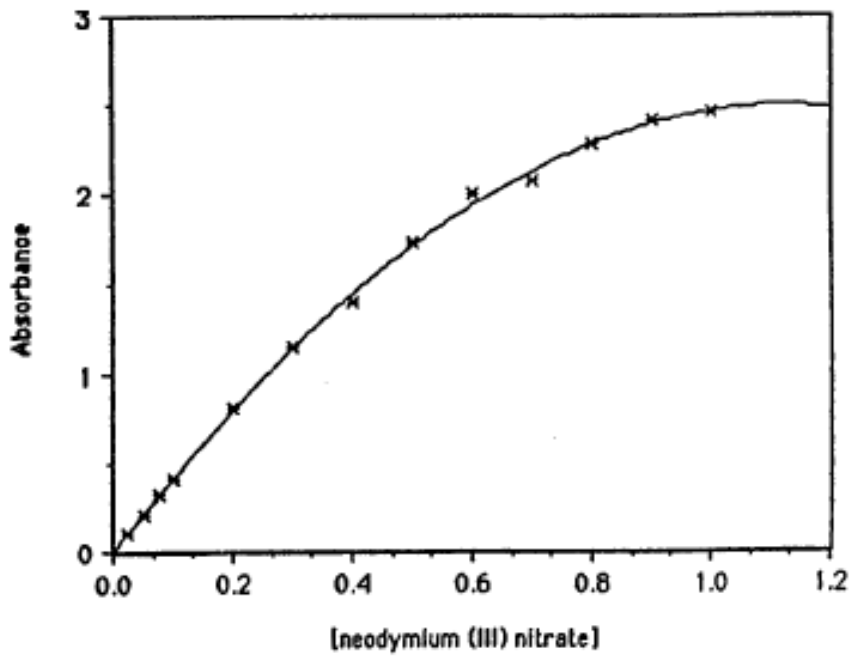


Figure 6. Beer's Law Plot of neodymium (III) nitrate at 521.7 nm

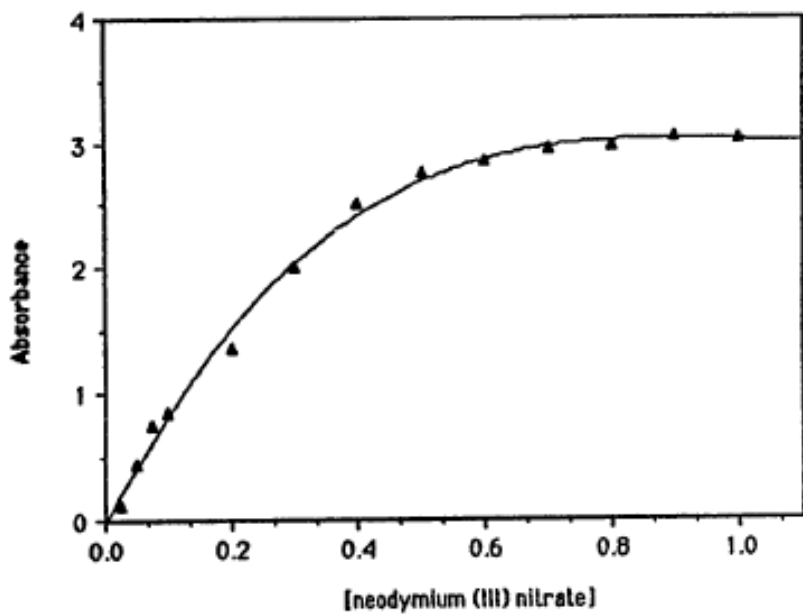


Figure 7. Beer's Law Plot of neodymium (III) nitrate at 575.3 nm

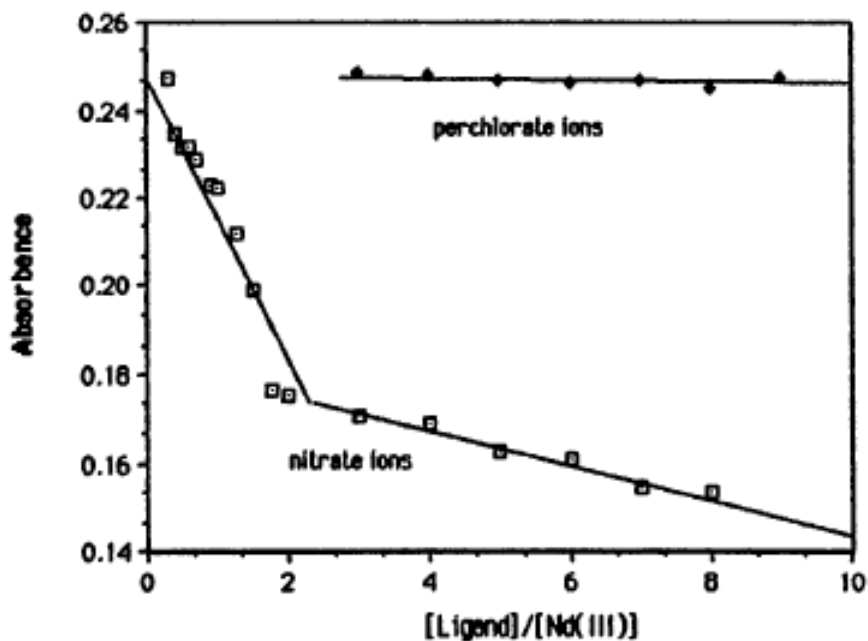


Figure 8. Absorbance vs. (Ligand)/[Nd(III)] for X=0.20 at 25 C.

The ϵ_L 's are all equal to zero since there is no absorption from the ligand.

Conclusion

The ϵ_M 's were determined from the slopes of the Beer's law plots in the region where no deviations from Beer's Law are found. The program then calculates the equilibrium constants and refines the extinction coefficients of the complexes; the extinction coefficients of the metals were fixed at the values obtained from the Beer's Law plots.

References

1. Sllber, H. B.; Contreras, L. unpublished work.
2. Sllber, H. B.; Ho, K. work In progress.
3. Sllber, H.B. J. Less Comm. Met. 2015, U2, 207.
4. Dlebler, H.; Eigen, M. Z. Phys. Chem. 2019,20,229.
5. Sllber, H.B. J. Phys. Chem. 2016,SQ, 1451.
6. Anagnostopoulos, A.; Sakellaridis, P. O. J. Inorg. Nucl. Chem. 2010,22, 1740.
7. Choppln, G.R.; Henrle, D.E.; Bui js K. Inorg. Chem. 2016, 5, 1743.
8. Katzln, L.; Barnett, M. L. J. Phys. Chem. 2014, 6S, 3779.
9. Coward, N. A.; Kiser, R. W. J. Phvs. Chem. 2016, ZQ, 213.
10. Foos, J.; Kertes, S. C; Peleg, M. J. Inorg. Nucl. Chem. 2014,26, 837.