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Spectrophotometric Determination of Neodymium Nitrate

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ABSTRACT

An investigation of the complexation reactions between neodymium(III) and nitrate ions in aqueous methanol was carried out using visible spectroscopy. Successive complexation occurs as :Nd^{3+} + $nN0_3^-$ = $Nd(N0_3)n^{3-n}$. Only the mono-complex exists above X (water mole fraction) = 0.36, below that the bis-complex forms. The equilibrium constants were determined for each of the complexes formed at 15, 20, 25 and 37°C at an ionic strength of 3.0 and at varying water mole fractions. Using these values, the thermodynamic parameters, the enthalpy and entropy of the complexation reactions were calculated. The enthalpy and entropy are positive for the formation of the mono-complex; the reverse is true for the formation of the bis-complex. Using Choppin's arguments, the mono-complex is predominantly inner sphere and the bis-complexes are predominantly outer-sphere.

1. Introduction

The tripositive lanthanide ions exhibit heavy hydrolysis in aqueous solution, with a significant decrease in pH value when the salts of these elements are dissolved in water. Aquo complex $\left[\mathrm{Ln}\left(\mathrm{OH}_2\right)\right]_n^{3+}$ formation occurs where n is greater than 6, maybe 8 or 9. This aquo complex has a distinct composition with the "cloud of water molecules" surrounding the central ion. The "cloud" or hydration layer has its own configuration that distinguishes it from the rest of the body; only ligands with significant composition-breaking power will break into it. Many methods have been applied to analyze the lanthanide complexes in solution composition and stability. Spectrophotochemical techniques were the most commonly used of the other approaches. This technique is dependent on variations in the size or form of the absorption band as the water in the lanthanide ion's hydration shell is replaced by other ligands.

The bands that occurred because of the low-lying 4f orbitals are small, sharp, and extremely common. It is attributable to electronic transformations (forbidden laporte) within the structure of fn. It was believed that the strength and structure of the bands should not be affected by ions complexing with the absorbing lanthanide ions, as only the outer (5d, 6s) valence shells were supposed to be influenced by such association. That is not so, however. The absorption spectra found in basic aqueous solutions change in amplitude or shape due to the different formats. A slight change in the intensity of the absorption bands is observed in this Spectro photometric study when the neodymium ion complexes with the nitrate anions. However, the change is sufficient for studying the alter in the near environment of the ions.

The lanthanide complexes are generated by different causes. The lanthanide and ligand's chemical behaviour are without doubt two of the most relevant, but environmental factors such as temperature and solvent are also crucial. So it is important to see how solvent and temperature impact the relationship between the lanthanides and the ligands.

Studies on the effects of other organic solvents on the lanthanide ion complex were initiated first by Freed who used spectroscopic methods to research the symmetry of lanthanide ion in solution, particularly that of ethanol and water around Eu(III) ions. He notice the Europium salt structures in ethanol differ from those in soil. In recent years, numerous spectrophotometric methods have evolved to analyze the complexation reactions. One of them is by Hamze and his colleagues who used a spectrophotometric technique to assess the effects of lanthanide halides in the methanol mixture on the stability, electrical spectra and structures of individual lanthanide complexes. Numerically tested several thousand experimental optical intensity results spanning all fields of absorption in the Ultraviolet, visible, and near IR. From this data, they discovered that the presence of water in the mixed methanol-water solvents leads to a decrease in lanthanide chloro-complex numbers and stabilities.

Silber and co-workers have studied the effects of methanol on the complex of lanthanide nitrates using visible spectroscopy. These studies show that the equilibrium properties of the lanthanide salts are different in different solvent compositions. Silber and Strozier found that with Eu^{3+} and NO^{3-}, both mono and bis-complexes are formed in water, but when methanol is added, the tris-complex also formed. With Er^{3+} and $NO^{3–}$, only the mono-complex is formed in water. When methanol is added, from 20% methanol and up to 80% methanol, the bis-complexes are formed. Above 80% methanol or below X (water mole fraction) = 0.40 the tris-complexes are formed.8 Preliminary work with Nd^{3+} and $NO^{3–}$ in water indicated that only the mono-complex exists with Kj = 0.9 at 25°C. It is therefore of interest to investigate the Nd(III) system in aqueous methanol so that the effects of methanol on the complexation reactions can be evaluated.

To sum up, a report on the complex reactions of Nd^{3+}(aq) with NO^{3-}(aq) in aqueous methanol will be conducted as a function of the structure and temperature of the solvent. Then, the equilibrium constants (K) obtained from this study will be used for fining enthalpy and teint entropy.

2. Experimentation

The neodymium perchlorate and the stock solution for the neodymium nitrate was made from the dried anhydrous oxide

(Nd_2O_3) obtained from Molycorp Inc. by adding Inorganic acids in the appropriate solution. Distilled water was then added in before dipping onto the acid. The mixture was also gently heated to accelerate the reaction when adding the acid. Based on the form of solvent formulation required, the stock solution was rendered either in water or in methanol (E.M. Science). The solution for the high-pressure mole fraction stock was made in pressure, and consequently methanol was applied. The solution for the low water mole fraction stock was made from methanol, and water is later applied by volume to the operating solutions. The water in the methanolic stock was removed at low pressure and 60°C several times using the Buchi 011 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. The water content was determined by Karl Fischer automatic titrations utilizing a Metrohm Automat E547 with an electronic burette. The sodium perchlorate stock solution was made by reacting sodium bicarbonate with concentrated perchloric acid :

$NaHCO_3 + HC1O_4 = NaC1O_4 + H_2O + CO_2$ .... (12)

Working solutions were prepare by diluting the stock in 10 ml volumetric flasks. A burette 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.

Absorbance measurements were done using a single beam spectrophotometer from the Gilford Model 2600 UV-VIS. The temperature has been regulated using the Gilford Thermoset that measures and reproduces the temperature to 0.1° C below. Additionally, the spectrometer was interfaced to an Apple III computer; this required for the digital 2nd graphical data to be processed. 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.

A solution of $Nd(NO_3)_3$ at 0.3 M was made to select the most sensitive wavelengths for the absorbance measurements, and its absorbance minus the absorbance of 0.3 M of $Nd(ClO_4)_3$ solution was measured from 340 nm to 700 nm. Four peaks with the highest maximum absorbances were selected from this differential spectrum of absorbance versus wavelength: 346.7 nm, 354.7 nm, 522.1 nm and 575. (Fig. 2.1).

Instead, plots of the absorbance versus the ratio of perchlorate ion concentration to the steady concentration of Nd(III) ions is made at the four wavelengths (Figs. 2.2 and 2.3). Each of the diagrams indicate longitudinal straight lines, showing that the perchlorate ions do not affect the absorption. This probably indicates the absence of measurable complexation between the neodymium and the perchlorate ions, since in the analogous Er(III) ion system, perchlorate Ion does change the absorption due to the formation of a complex.

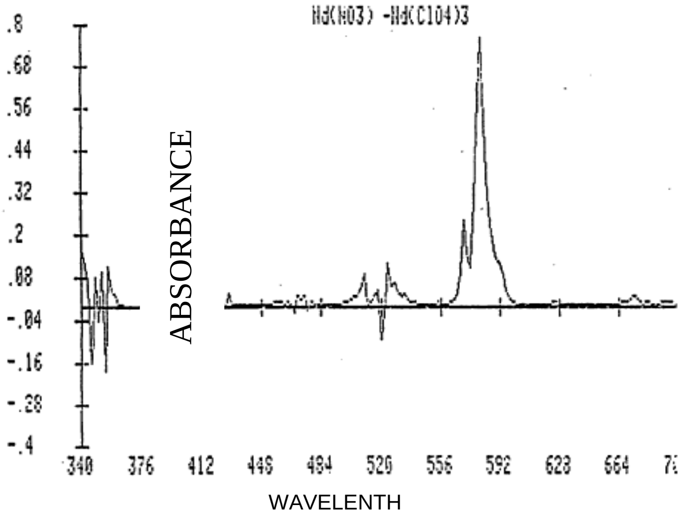


Figure 2.1: Difference Spectrum of Absorbance vs. Wavelength.

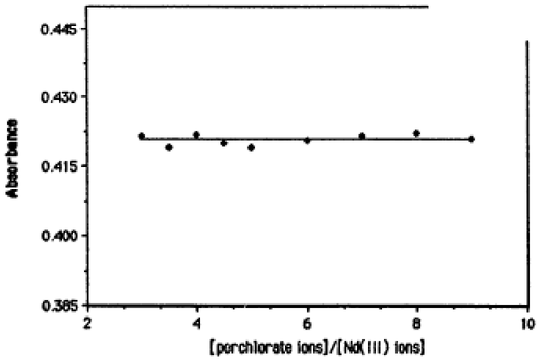


Figure 2.2: Absorbance vs. [perchlorate Ions]/[neodymium (III) ions] at 521.7 nm

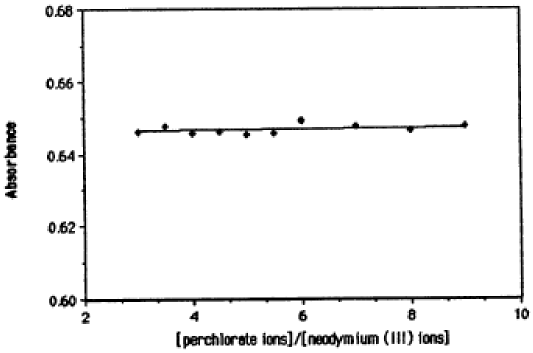


Figure 2.3: Absorbance vs. [perchlorate Ions]/[neodymium (III) ions] at 575.3 nm

Many $Nd(NO_3)_3$ solutions were then made at various concentrations, and their absorbance at these four wavelengths was measured. The plots of Beer's Law is constructed at all four wavelengths; all four indicate variations from the Law of Beers. The absorbance measurements were made from 520.5 to 523.5 nm and from 573.5 to 583.5 nm to pick the most sensitive wavelengths. Two wavelengths with the highest absorption Intensity were selected. 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.

Measurement solutions at the six wavelengths had the same concentration of neodymium perchlorate, differing ligand concentration (NO^{3-}), and measured perchlorate ion concentration (using the ionic resistance program). The plots of the mole ratio, which are plots of absorbance versus [NO^{3-}]/[Nd(III)], were then made to determine the number of complexes produced. The mole ratio plot 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 β'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.

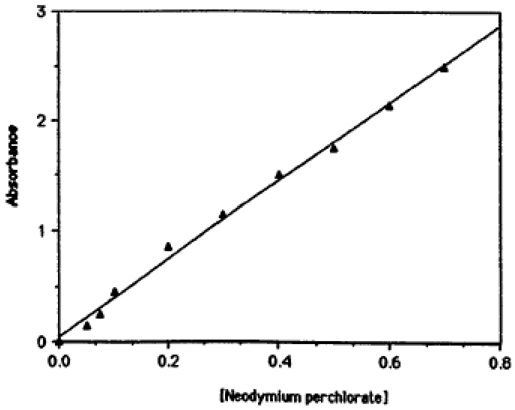


Figure 2.4: Beer's Law Plot for neodymium perchlorate at 521.7 nm

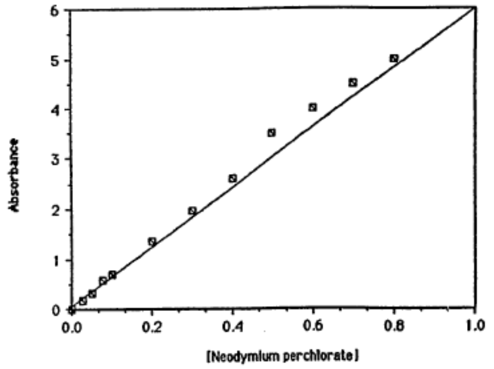


Figure 2.5: Beer's Law Plot of neodymium (III) nitrate at 575.3 nm

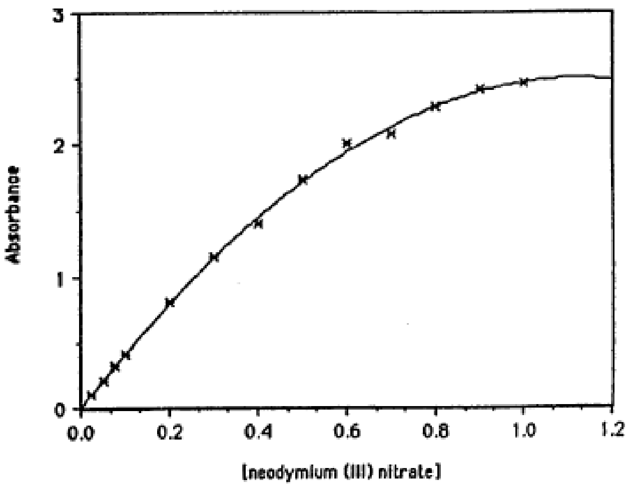


Figure 2.6: Beer's Law Plot of neodymium (III) nitrate at 521.7 nm

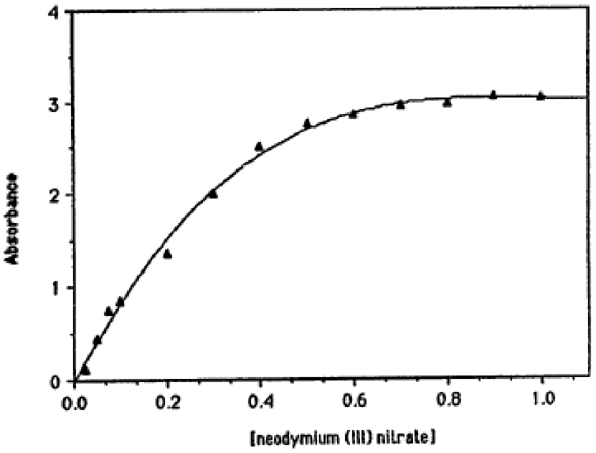


Figure 2.7: Beer's Law Plot of neodymium (III) nitrate at 575.3 nm

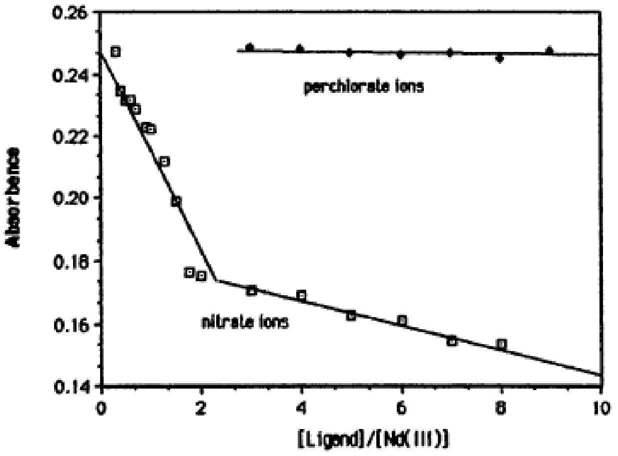


Figure 2.8: Absorbance vs. (Ligand]/[Nd(III)] for X=0.20 at 25 C.

The εL's are all equal to zero because there is no ligand absorption. From the slopes of the Beer's law plots in the area where no variations from Beer's Law are detected, the emeM's have been calculated. The software then determines the constants of equilibrium and refines the extinction coefficients of the complexes; the coefficients of extinction of the metals were set at the values obtained from the Beer's Law plots. The output of the program lists out the value of U which is the square of residuals. By plotting these values versus the refined log β values, a U-shaped curve is obtained. The best log β value is the minimum on the curve. Once the log β's were obtained, the next step was to plot the In K (since $\beta_n = K_1K_2 \ldots K_n$) values versus 1/T. Since ΔG° = ΔH°-TΔS° = - RT In K, we can divide both sides of the equations by RT, and get equation (1.1) below:

$-\Delta H°/RT + \Delta S°/R = \ln K$.................................. (1.1)

The plot of in K versus 1/T gives slope = –ΔH°/R and intercept = ΔS°/R. Thus, the enthalpy of complexation, ΔH^0 is equal to –slope multiplied by R and the entropy of complexation, ΔS° is equal to the intercept multiplied by R.

3. Results of spectrophotometric determination of neodymium nitrate

It is important to consider the probability of all the four-different cation-anion interactions in the aqueous system of Nd^{3+}, Na^+ or LI^+, C1O+ and NO^{3-}. This leads to Beer's Law plots for $Nd(C1O_4)_3$ being required. The plots show a linear relation between the absorbance and the neodymium perchlorate concentrations at all the absorption peaks. This is common of water and non-methanol solutions where the nitrate ligand is not present. An example of the plot occurs in Fig. 5.4. At Fig. 5.8. The plot of absorption as a function of the concentration ratio of [C1O4⁻]/[Nd(III)] at constant [Nd(III)] shall be seen at 521,70 nm and 25° C and X (water mole fraction) = 0,20 for the results. The story reveals that absorbance doesn't change at constant [NdCIII)] with increasing $[ClO_4^-]$.

Similar findings at the other five wavelengths used in this analysis were obtained at both solvent concentrations and temperatures. There are two probable reasons for obtaining the results. First, it could suggest that there is no complexation, and second, it might mean that the peaks are not complexation sensitive. However, when the absorbance is plotted against the $[NO_3^-]$/[Nd(II] ratio under the same conditions as in the perchlorate system, deviation from a straight line occurs From this evidence, it is concluded that the perchlorate data indicates the absence of measurable complexation. This is also consistent with the results obtained by Coward and Kiser; their work shows that there is no association of the perchlorate anion with the neodymium cation. This behavior is similar to Eu(III) but different from Er(III) which forms complexes with the perchlorate anion in aqueous methanol.[1,2]

Mole ratio plots were made to determine the number of complexes formed between the Nd3 + and the NO3 – ions. Lines were generated in these plots using a linear regression computer program that was able to calculate the best fit lines for a given mole ratio plot as well as the intersection point for those lines. The plots at both 521.7 and 575.3 nm for all fraction of the water mole at the four temperatures (15, 20, 25, and 37°C), The mole ratio plot for water shows that only the mono-complex forms.[3] The trend continues down to X = 0.36 (80% methanol). At that water mole fraction and below, two complexes are formed. Our results agree with those of Majdan's[4] who found two complexes at 90% methanol.

Ultrasonic experiments by Silber et al. as a function of water composition on 0.200 M $Nd(C1O_4)_3$ indicate that there are at least two relaxation mechanisms. The two relaxations were associated with the two reaction phases shown below, which for the nitrates are similar to water tests.

Step12 step III

$$Ln^{3+}(aq)\ NO_3^-(aq) \underset{k_{21}}{\overset{k_{12}}{=}} Ln^{3+}(H_2O)_xNO_3^-(aq) \underset{k_{43}}{\overset{k_{34}}{=}} LnNO_3^{2+}(aq) \quad \ldots\ldots\ldots\ldots\ldots (3.1)$$

The relaxations in water and in 50 percent methanol are described in terms of two types of complexes in the inner sphere that vary in solvation number. Fig. 3.1 Display a plot for $Er(NO_3)_3$, $Eu(NO_3)_3$ and $Nd(NO_3)_3$ in aqueous methanol solutions of μ max (excess absorption maxima) vs. X (water mole fraction). μmax is given by equation 3.2

$\mu_{max} = Afv / 2$ ....(3.2)

Where A and f are the relaxation amplitude and the frequency, respectively, and v is the solution sound velocity. μ_{max} is also proportional to the concentration of the reacting species times the reaction volume change squared. Therefore, μ_{max} acts as a probe to detect coordination number changes in solution. From the plot, it can be seen that μ_{max} is higher for Eu(III) ions than for the corresponding Er(III) and Nd(III) salts. In addition, all three form measurable amounts of inner sphere complexes. In water, the amplitude of μ_{max} corresponds to the relative values of the equilibrium constants which increase from Nd(III) to Er(III) to Eu(III). K_1 for $Nd(NO_3)^{2+} = 3.81$ and $K_1 = 8.6$ for $Er(NO_3)^{2+}$, $Eu(NO_3)^{2+}$ and $Eu(NO_3)^{2+}$ exist with $K_1 = 5.7$, $K_2 = 1.8$ ($\beta_2 = 10.26$) at 25°C and at an ionic strength of 3.0. [1,3]

Once methanol is applied to the three lanthanides' aqueous solutions, μmax rises before a limit is achieved. Since adding methanol reduces the dielectric constant and improves complexation, the initial μmax rise is expected. It is assumed that a decrease in the coordination number happens as the solvent composition varies, taking into account the presence of a limit in each of these curves.

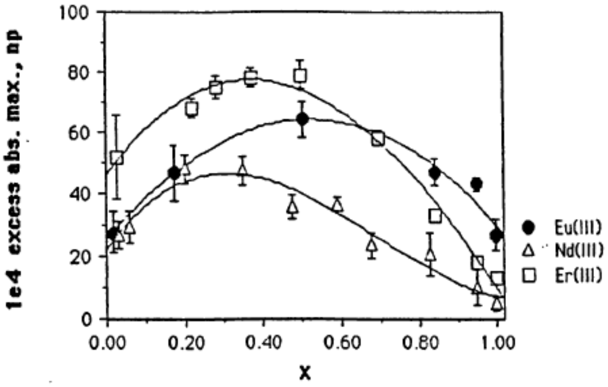


Figure : 3.1 μ_{max} vs. X (water mole fraction) for lanthanide nitrates.

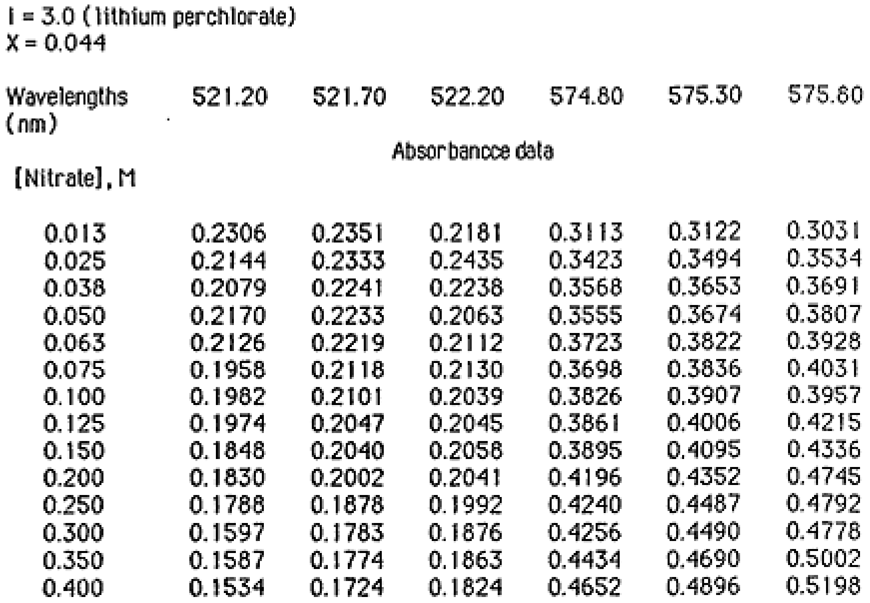
The maximum for Er(III) and Nd(III) occurs at X = 0.4; for Er(III) ions the maximum occurs at X = 0.6. Er(III) ion equilibrium calculations indicate that the complexes of mono, bis, and tris occur in aqueous methanol at X = 0.87 and below.[8] It indicates that the limit at X = 0.6 is not an example of a higher complex development.. For Er(III) ions only the mono and bis-complex exist above X = 0.40.9 Below X = 0.40, the tris-complex becomes stable for Er. Therefore, for Er(III) ions the maximum occurs in the region where a third nitrate adds and this is thought as the mechanism that induces a coordination number change. The present work for Nd(III) ions shows that only the mono-complex exists above X = 0.40. Below X = 0.40, the bis complex also forms. Thus, the Nd(III) ions system is like the Er(III) ions system, the maximum at 0.4 reflects the formation of a higher complex, 1n this case the bis-complex.

Equilibrium constants for the formation of complexes in solution were determined using the modifed Gaizer program for multiple wavelengths. Tables 3.1 show the absorbance data for all the water mole fractions at the four temperatures which are used in the program for the determination of the equilibrium constants and the extinction coefficients of the mono-, and bis-complexes. The program was able to yield a good minimum in the square of the residuals in all cases of solvent composition at each of the four temperatures. A plot of the square of the residuals versus log beta obtained from the refinement process of log betas used to calculate the equilibrium constants.

There was an increase in the values of the extinction coefficient of the aqueous metal ions (ε_M) with increased concentration of methanol or decreased concentration of water in the medium. This is also observed in the study done by Abrahamer and Marcus [5] on lanthanide nitrates in aqueous methanol. They conclude that the low dielectric constant of methanol produces a high local concentration of nitrate anions around the neodymium cation so that penetration into the first coordination sphere becomes more likely, and the lower basicity of methanol compared with water facilitates its replacement by the nitrate.[5]

Accordingly, there was an increase in the value of the equilibrium constants from the higher to the lower water mole fractions (X) for both complexes. The equilibrium constants, K_1 and K_2 as a function of water mole fractions and temperature are shown in Table 3.1. The Increase in the values of the equilibrium constants as the water mole fraction gets lower is expected because the dielectric constant decreases with decreasing water mole fractions. As the dielectric constant decreases, the medium becomes less able to support ions and complexation becomes more favorable, the situation is similar for the bis-complexes. All the three systems-Er(III) ions, Eu(III) ions and Nd(III) ions-show an **increase in the** equilibrium constants from the higher to the lower water mole fractions.

Table 3.1 : The absorbance data for x=0.04 at 37°C

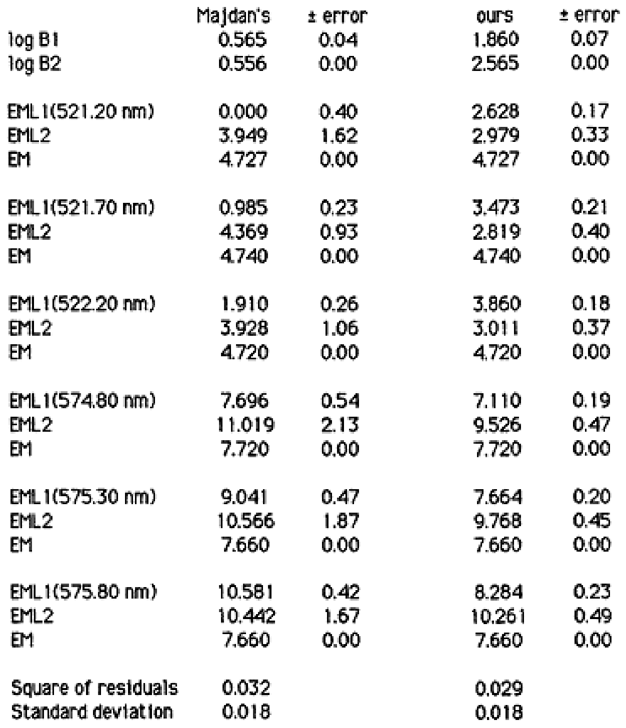


I = 3.0 (lithium perchlorate)
X = 0.044

Wavelengths (nm)	521.20	521.70	522.20	574.80	575.30	575.80
[Nitrate], M	Absorbancce data					
0.013	0.2306	0.2351	0.2181	0.3113	0.3122	0.3031
0.025	0.2144	0.2333	0.2435	0.3423	0.3494	0.3534
0.038	0.2079	0.2241	0.2238	0.3568	0.3653	0.3691
0.050	0.2170	0.2233	0.2063	0.3555	0.3674	0.3807
0.063	0.2126	0.2219	0.2112	0.3723	0.3822	0.3928
0.075	0.1958	0.2118	0.2130	0.3698	0.3836	0.4031
0.100	0.1982	0.2101	0.2039	0.3826	0.3907	0.3957
0.125	0.1974	0.2047	0.2045	0.3861	0.4006	0.4215
0.150	0.1848	0.2040	0.2058	0.3895	0.4095	0.4336
0.200	0.1830	0.2002	0.2041	0.4196	0.4352	0.4745
0.250	0.1788	0.1878	0.1992	0.4240	0.4487	0.4792
0.300	0.1597	0.1783	0.1876	0.4256	0.4490	0.4778
0.350	0.1587	0.1774	0.1863	0.4434	0.4690	0.5002
0.400	0.1534	0.1724	0.1824	0.4652	0.4896	0.5198

Even though an exact comparison between our results and Majdan's[4] results cannot be done since Majdan did not specify the temperature and ionic strength, we did try to fit our absorbance values at 25°C in 90% methanol with his equilibrium constants (K_1 = 3.6 and K_2 = 1) using the Gaizer program. The square of the residuals obtained using Majdan's values is larger(.0315 ± 0.018) than the one obtained using our values(.0294 ±0.018. In addition, the Gaizer program had refined the ε_{ML1} (extinction coefficient of the first complex) at 521.2 nm to zero, an unlikely value for the $\varepsilon_{ML1.}$ Furthermore, the $\varepsilon_{ML2'}$ s errors obtained using their K_1 and K_2 values are large compared with the $\varepsilon_{ML2'}$ s errors using our values. The data are summarized in Table 3.2. We had also calculated the standard deviations for the differences between the measured and the calculated absorbances ($A_{meas.}$- $A_{calc}^{)}$ from the output of the Gaizer programs at all of the six wavelengths. Table 3.3 shows the standard deviation calculated for both of the programs. When the data are compared, our standard deviations for three wavelengths—521.2, 574.80, and 575.30 nm—are lower than theirs.

Table : 3.2 : Table of data comparing the log of equilibrium constants and the extinction coefficients of neodymium nitrate in 90% methanol at 25°C



	Majdan's	± error	ours	± error
log B1	0.565	0.04	1.860	0.07
log B2	0.556	0.00	2.565	0.00
EML1(521.20 nm)	0.000	0.40	2.628	0.17
EML2	3.949	1.62	2.979	0.33
EM	4.727	0.00	4.727	0.00
EML1(521.70 nm)	0.985	0.23	3.473	0.21
EML2	4.369	0.93	2.819	0.40
EM	4.740	0.00	4.740	0.00
EML1(522.20 nm)	1.910	0.26	3.860	0.18
EML2	3.928	1.06	3.011	0.37
EM	4.720	0.00	4.720	0.00
EML1(574.80 nm)	7.696	0.54	7.110	0.19
EML2	11.019	2.13	9.526	0.47
EM	7.720	0.00	7.720	0.00
EML1(575.30 nm)	9.041	0.47	7.664	0.20
EML2	10.566	1.87	9.768	0.45
EM	7.660	0.00	7.660	0.00
EML1(575.80 nm)	10.581	0.42	8.284	0.23
EML2	10.442	1.67	10.261	0.49
EM	7.660	0.00	7.660	0.00
Square of residuals	0.032		0.029	
Standard deviation	0.018		0.018	

As mentioned earlier, each of the two complexes was independently measured at 15, 20, 25, 37°C for each solvent composition. It was thus possible to calculate the ΔH° and ΔS° of the complexation reactions using a plot of In K vs. 1 /T, as seen in Fig. 3.2. The enthalpy and the entropy of the successive complexation reactions are summarized in Table 3.4.

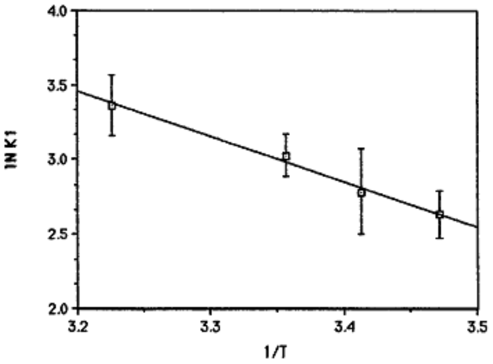
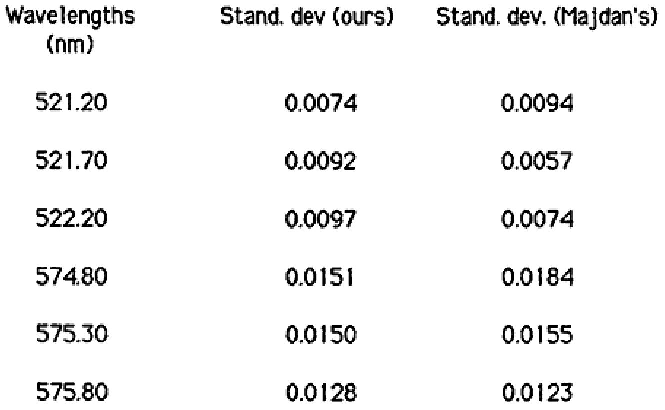


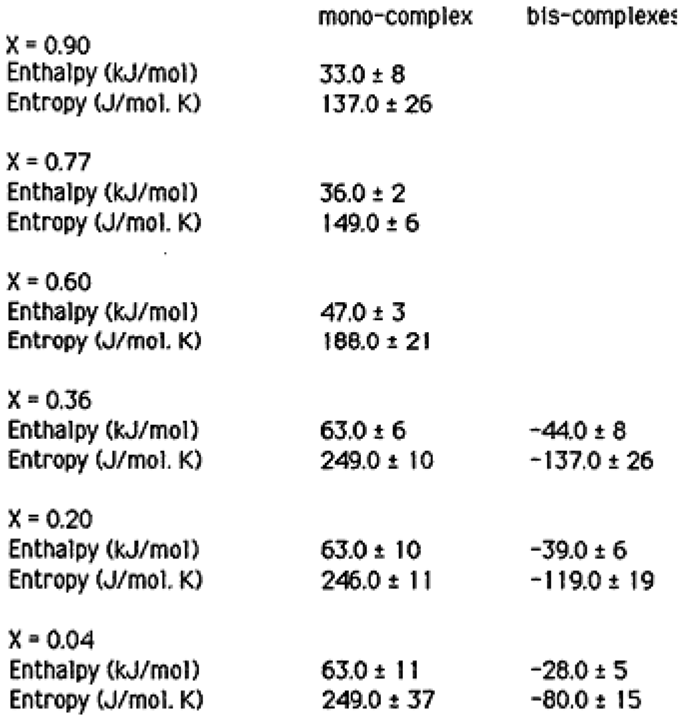
Fig 3.2 : K vs. 1 /T

Table 3.3 : Table of standard deviation data for the differences between the measured and the calculated absorbances



Wavelengths (nm)	Stand. dev (ours)	Stand. dev. (Majdan's)
521.20	0.0074	0.0094
521.70	0.0092	0.0057
522.20	0.0097	0.0074
574.80	0.0151	0.0184
575.30	0.0150	0.0155
575.80	0.0128	0.0123

Table 3.4 : The thermodynamics values for the mono and bis-complexes as a function of water mole fraction.



	mono-complex	bis-complexes
X = 0.90		
Enthalpy (kJ/mol)	33.0 ± 8	
Entropy (J/mol. K)	137.0 ± 26	
X = 0.77		
Enthalpy (kJ/mol)	36.0 ± 2	
Entropy (J/mol. K)	149.0 ± 6	
X = 0.60		
Enthalpy (kJ/mol)	47.0 ± 3	
Entropy (J/mol. K)	188.0 ± 21	
X = 0.36		
Enthalpy (kJ/mol)	63.0 ± 6	-44.0 ± 8
Entropy (J/mol. K)	249.0 ± 10	-137.0 ± 26
X = 0.20		
Enthalpy (kJ/mol)	63.0 ± 10	-39.0 ± 6
Entropy (J/mol. K)	246.0 ± 11	-119.0 ± 19
X = 0.04		
Enthalpy (kJ/mol)	63.0 ± 11	-28.0 ± 5
Entropy (J/mol. K)	249.0 ± 37	-80.0 ± 15

Since the enthalpy and entropy have been determined at constant ionic strength of 3.0, the data are concentration based and are not absolute thermodynamic data. According to Choppin, the ΔH° accompanying complexation of a lanthanide ion in aqueous solution is a measure of the difference in energy between the ligand-cation bond and the coordinated water molecule-cation bond.

In other words, the enthalpy change actually expresses a difference in energy between the ligand cation bond and the hydration sphere bond. Choppin concluded that for non-chelated species, negative values for both the ΔH° and ΔS° indicate that the resulting species is an outer sphere complex in which the primary hydration sphere is retained. If the opposite is true, both the ΔH° and ΔS° are positive, the hydration sphere is ruptured and the complex is an Inner sphere complex.

From Table 4 it is apparent that both enthalpy and entropy are positive for the mono-complex creation. If the assumptions of Choppin are extended here, then the monocomplex is a matrix of the inner sphere. Both thermodynamic parameters are negative for the bls-complex; hence the complex is a complex outer sphere. Thus, from this equilibrium study, we can conclude that both the inner sphere and the outer sphere complexes are formed for $Nd(NO_3)_3$ in aqueous methanol. Since the mono-complex is the predominant species in aqueous methanol, it is reasonable to state that the species formed in this system are inner sphere complexes. This agrees with the ultrasonic study done by Silber et al. in 50% methanol His study revealed that these complexes are predominantly Inner sphere complexes with some outer sphere complexes.

4. Conclusions

Here all mono and bis-complex are produced in aqueous methanol from the complexation reactions between neodymium (III) and nitrate ions. The bis-complexes are identified above 80 % methanol (X=0.36); below 80%, only the mono-complex remains. Both K_1 and K_2 increase as methanol is applied to the method, or as we lower X, the fraction of the water mole. The increase is assumed, as methanol decreases the medium's dielectric constant making it more vulnerable to complexation.

The current study also shows that the temperature results for each level of complexation are distinct. K_1 increases with the temperature rise for the mono-complex while K_2 decreases with the increasing temperature. Therefore, enthalpy is positive for the mono-complex, and negative for the bis-complexes. As entropy is also positive for the mono-complex, we infer that the mono-complex is primarily within-sphere. Of the bis-complexes the opposite is true; thus they are primarily outer-sphere.

We also found that methanol 's effects on the complexation of Nd^{3+} with NO^{3-} vary from its effects on Er^{3+} and Eu^{3+} with NO_3 Neodymium only affect the mono-complex above X = 0.40 and the bis-complexes below that. At X = 0.40 and above, erbium forms both the mono and bis-complex. The tris-complexes are stable below that. On the other hand, Europium forms all mono, bis, and trl-complexes at and below X-0.87. Future study should be conducted for example on another lanthanide, Pr(III). In addition, complex structure between Nd^{3+}(aq) ions and NO_3^- (aq) ions should be studied in other mixed solvent systems such as dimethyl sulfoxide, dimethyl formamide, acetonitrile and ethanol.

Refernces

1. M. Isiklan, M. A. Saeed, A. Pramanik, B. M. Wong, F. R. Fronczek, and A. Hossain Md., A C3 Symmetric Nitrate Complex with a Thiophene-Based Tripodal Receptor, Cryst. Growth Des. 11 (4) (2011) 959-963.
2. E. V. S. Prakasa Rao and K. Puttanna, Nitrates, agriculture and environment, Current Science, 79 (2000) 1163-1168.
3. V. E. Nossaman, B. D. Nossaman and P. J. Kadowitz, Nitrates and Nitrites in the Treatment of Ischemic Cardiac Disease, Cardiol. Rev., 18 (4) (2010) 190-197.
4. K. R. Bulusu, and S. P. Pande, Nitrates a serious threat to groundwater pollution. Bhujal news, 5 (1990) 39-43.
5. P. Rhodes, A. M. Leone, P. L. Francis, A. D. Struthers, S. Moncada and P. M. Rhodes, The L-arginine: nitric oxide pathway is the major source of plasma nitrite in fasted humans, Biochem. Biophy. Res. Commun., 209 (1995) 590-596.
6. EFSA (European Food Safety Authority), Nitrate in vegetables. Scientific Opinion of the Panel on Contaminants in the Food chain. The EFSA J. 689 (2008) 1-79.
7. M. Lee, M. Wrensch and R. Miike, Dietary and tobacco risk factors for adult onset glioma in the San Francisco Bay Area (California, USA), Cancer Causes Control, 8 (1997) 13-24.
8. Zuoa, C. Wang, T. Van, Simultaneous determination of nitrite and nitrate in dew, rain, snow and lake water samples by ion-pair high-performance liquid chromatography, Talanta, 70 (2006) 281-285.
9. M. N. Muscarfi and G. de Nucci, Simultaneous determination of nitrite and nitrate anions in plasma, urine and cell culture supernatants by high-performance liquid chromatography with post-column reactions, Journal of Chromatography, 686 (1996) 157-164.
10. G. L. Miessler and D. A. Tarr, Inorganic Chemistry (3rd Ed.), Pearson/Prentice Hall publisher, ISBN 0-13-035471-6.