SIGNIFICANCE OF SPECTROPHOTOMETRY METHOD IN COMPLEX NUMBERS

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Abstract

In the aqueous system of Nd^{3+}, Na^+ or LI^+, $C1O_4^-$ and NO_3^-, it is important to consider the possibility of all the four-different cation-anion interactions. This leads to the necessity of Beer's Law plots for $Nd(C1O_4)_3$. The plots at all the absorption peaks show a linear relationship between the absorbance and the concentration of the neodymium perchlorate. This is true in water and in water-methanol solutions in the absence of the nitrate ligand. The plot shows that there is no change in absorbance at constant [NdCIII)] with increasing [CIO_4-].
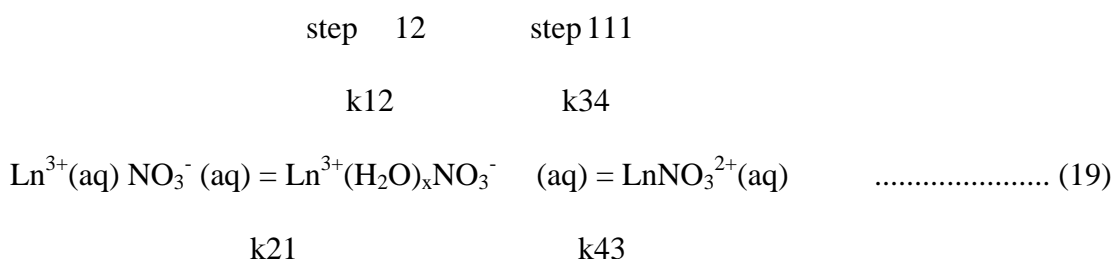
Introduction

Similar results were obtained at all the other five wavelengths used in this study at all solvent compositions and temperatures. There are two probable reasons for the results obtained. First, it could Indicate that there is no complexation and second, it could mean that the peaks are not sensitive to complexation. 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 (Fig. 8) 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.[8,22]

To determine the number of complexes formed between the Nd^{3+} and the NO_3^- ions, mole ratio plots were made. Lines in these plots were generated using a linear regression computer program which was able to calculate the lines of the best fit for a given mole ratio plot as well as the intersection point of those lines. The plots at both the 521.7 and 575.3 nm for all the water mole fractions at the four temperatures (15, 20, 25, and 37° C) are included in (Appendix A), Figs. 24 to 47. The mole ratio plot for water shows that only the mono-complex forms.[10] The trend continues down to X = 0.36 (80% methanol). At that water mole fraction and below, two complexes are formed (Figs. 36-39). Our results agree with those of Majdan's who found two complexes at 90% methanol.

Ultrasonic measurements by Silber et al. on 0.200 M $Nd(ClO_4)_3$ as a function of water composition show that at least two relaxation processes exist. The two relaxations were correlated with the two reaction steps shown below, which are analogous to the results in water for the nitrates.

$$step \quad 12 \qquad step \, 111$$

$$k12 \qquad\qquad k34$$

$$Ln^{3+}(aq) \; NO_3^- \; (aq) = Ln^{3+}(H_2O)_xNO_3^- \quad (aq) = LnNO_3^{2+}(aq) \qquad \text{.....................} (19)$$

$$k21 \qquad\qquad k43$$

The relaxations in water and in 50% methanol are interpreted in terms of two forms of inner sphere complexes which differ in solvation number. Fig. 9 shows a plot of μ max (excess absorption maxima) vs. X (water mole fraction) for $Er(NO_3)_3$, $Eu(NO_3)_3$ and $Nd(NO_3)_3$ in aqueous methanol solutions.]imax is given by equation 29

$$\mu_{max} = Afv \, / \, 2 \quad \text{....................................} (29)$$

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 (β_2 = 10.26) at 25°C and at an ionic strength of 3.0.[10 24-8]

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When methanol is added to aqueous solutions of all the three lanthanides, μ_{max} increases until it reaches a maximum. Since the addition of methanol lowers the dielectric constant and increases complexation, the initial increase in μ_{max} is expected. it is believed that a coordination number change takes place as the solvent composition changes, judging from the existence of a maximum in each of these curves.
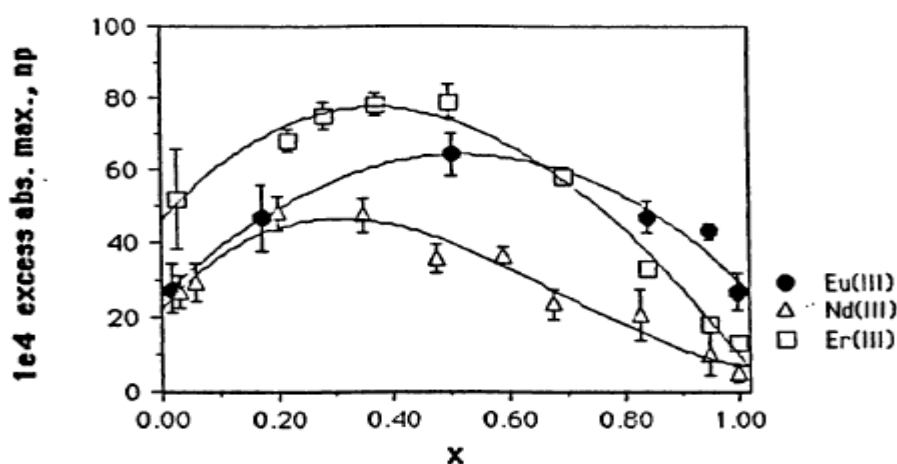

Figure 9. μ_{max} vs. X (water mole fraction) for lanthanide nitrates.

For Er(III) and Nd(III) the maximum occurs at X = 0.4; for Er(III) ions the maximum takes place at X = 0.6. The equilibrium measurements for Er(III) ions reveal that the mono, bis and tris complexes exist in aqueous methanol at X = 0.87 and below.8 This shows that the maximum at X = 0.6 is not an indication of a higher complex forming. 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 5-28 in Appendix B 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 is shown in Fig.10. The equilibrium constants and the extinction coefficients of both the aqueous metal ions and the complexes are listed in Tables 29 -34 in Appendix B.

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 Marcus5 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 1. A plot of K_1 vs. X at 25°C is presented in Fig. 11. In Fig. 12, plots of K_1 vs. X for $Er(NO_3)_3$, $Eu(NO_3)_3$ and $Nd(NO_3)_3$ at 25°C are shown. Similar plots for K_2 are shown in Figs. 13-14. The Increase in the values of the equilibrium constants as the water mole
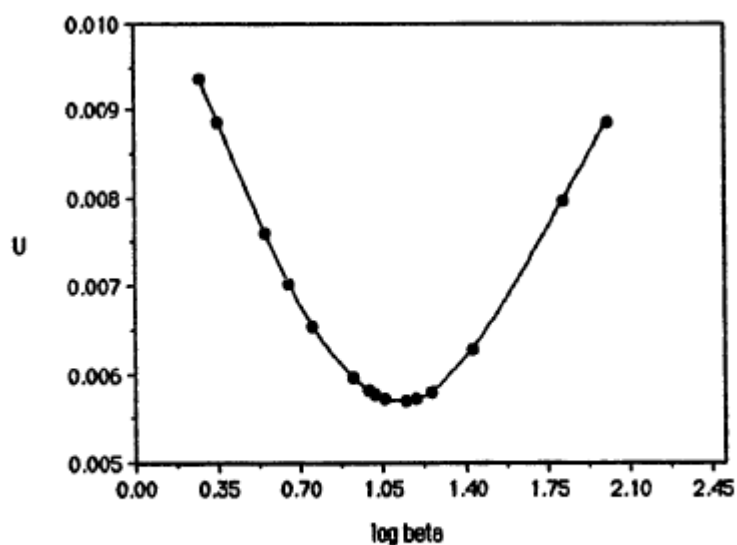

Figure 10. U vs. log beta for X = 0.90 at 15 C

Table 1

Equilibrium constants of the complexes as a function of temperature and water mole fractions

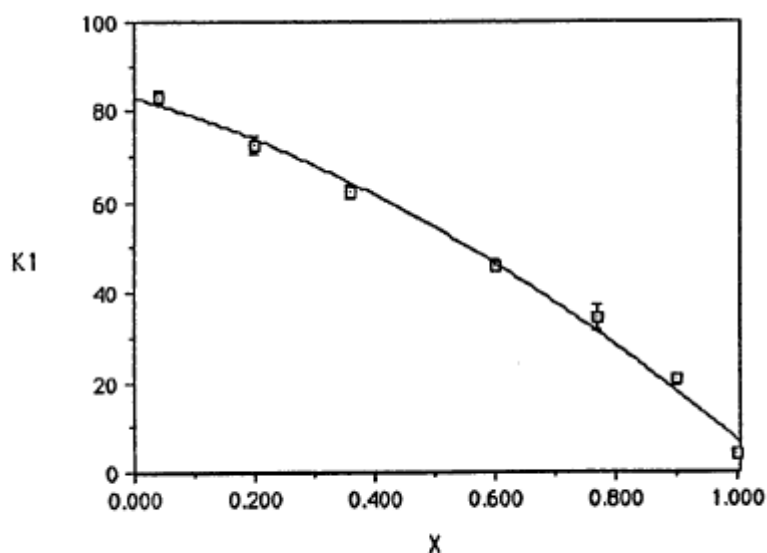| Temp. (Celcius)	15	20	25	37
Xw = 0.90				
K1	10.09 ±1.2	16.23 ± 1.3	20.67 ± 1.2	28.86 ± 1.2
Xw = 0.77				
K1	22.29± 1.2	27.08 ± 1.2	34.32 ± 1.2	63.10± 1.2
Xw = 0.60				
K1	23.17± 1.2	30.09 ± 1.2	45.98 ± 1.3	90.16± 1.2
Xw = 0.36				
K1	25.53 ± 1.7	39.28 ± 1.6	62.34 ± 1.4	166.73 ± 1.5
K2	7.33 ± 1.4	6.49 ± 1.3	4.12 ± 1.1	2.09 ± 1.1
Xw = 0.20				
K1	27.26 ± 1.5	45.12 ± 1.3	72.43 ± 1.8	176.32 ± 1.5
K2	7.55 ± 1.0	7.03 ± 1.05	5.07 ± 1.1	2.48 ± 1.5
Xw = 0.04				
K1	31.72 ± 1.3	54.85 ± 2.0	83.12 ± 1.4	210.91± 1.5
K2	8.13 ± 1.0	7.94 ± 1.0	5.56 ± 1.0	3.75 ± 1.0

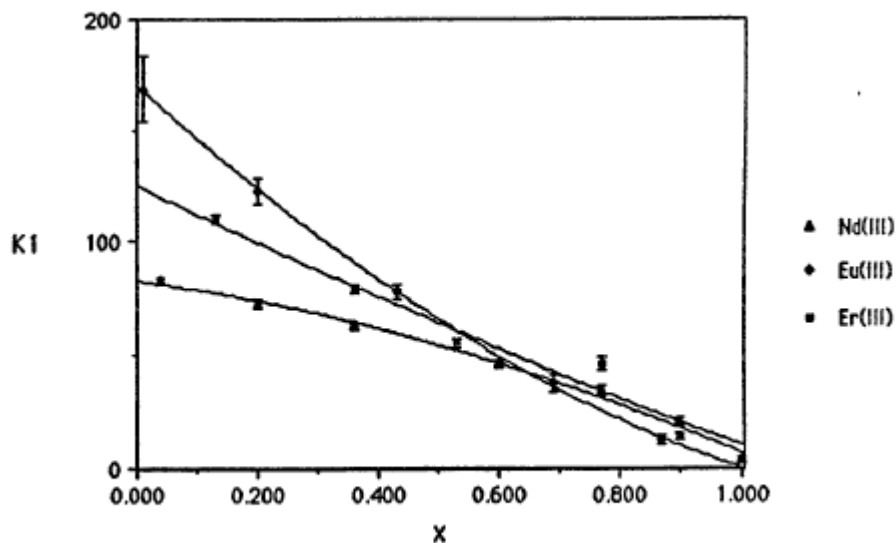Figure 11. K1 for neodymium nitrate vs. X at 25°C

Figure 12. Lanthanide nitrate mono-complexes at 25 ° C

Even though an exact comparison between our results and Majdan's[2] 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 ε_{ML1}. Furthermore, the ε_{ML2}, s errors obtained using their K_1 and K_2 values are large compared with the ε_{ML2}, s errors using our values. The data are summarized in Table 2.

Discussion

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 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 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 $\Delta H°$ and $\Delta S°$ of the complexation reactions using a plot of In K vs. 1 /T, as seen in Fig. 15. The enthalpy and the entropy of the successive complexation reactions are summarized in Table 4. The enthalpy for the mono-complex is displayed graphically in Fig. 16 and the entropy in Fig. 17. Fig. 18 and Fig. 19 show the combined data of the enthalpy and entropy for the mono-complexes of Er(III), Eu(III) and Nd(III) nitrate in aqueous methanol. The data for the bis-complexes are shown in Figs. 20-23.

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 $\Delta H°$ 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 $\Delta H°$ and $\Delta S°$ 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 $\Delta H°$ and $\Delta S°$ are positive, the hydration sphere is ruptured and the complex is an Inner sphere complex.

Both the mono and the bis-complexes are formed from the complexation reactions between neodymium (III) and nitrate ions in aqueous methanol. The bis-complexes are found above 80% methanol (X=0.36); below 80% methanol only the mono-complex exists.

Both K_1 and K_2 increase as methanol is added to the system or as we lower X, the water mole fraction. The increase is expected, since methanol lowers the dielectric constant of the medium making it more susceptible to complexation.

The present work also shows that the effects of temperature are different for each complexation step. K_1 for the mono-complex increases with the increase in temperature, whereas K_2 decreases with the increase in temperature. The enthalpy is therefore positive for the mono-complex and negative for the bis-complexes. Since the entropy is also positive for the mono-complex, we conclude that the mono-complex is predominantly inner-sphere. The reverse is true for the bis-complexes; therefore, they are predominantly outer-sphere.

Conclusion

We have also observed that the effects of methanol on the complexation of Nd^{3+} with NO_3^- are different from its effects on Er^{3+} and Eu^{3+} with NO_3 Neodymium forms only the mono-complex above X = 0.40 and bis-complexes below that. Erbium forms both the mono and the bis-complexes at X = 0.40 and above. Below that the tris-complexes are stable. **Europium,** on the other hand forms all mono, bis and trls-complexes at and below X - 0.87. Future study should be carried out on a different lanthanide, Pr(III) for example. In addition, complex formation between Nd^{3+}(aq) ions and NO_3^- (aq) ions in other mixed solvent systems such as dimethyl sulfoxide, dimethyl formamide, acetonitrile and ethanol should also be investigated.

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