USAGE OF SPECTROPHOTOMETRY METHOD IN COMPLEX NUMBERS

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Abstract

In aqueous solution the tri-positive lanthanide ions show strong hydrolysis with a definite decrease in the pH value when the salts of these elements are dissolved in water. This aquo complex with the "cloud of water molecules" surrounding the central ion has a definite structure. The "cloud" or the hydration shell has its own geometry which separates it from the rest of the water; only ligands with strong structure-breaking influence can break into it.

Various methods have been applied to examine the structure and stability of lanthanide complexes in solution. Among the many methods, Spectro photo chemical methods have been most frequently employed. These methods are based on the change in the intensity or shape of the absorption bands when the water in the hydration shell of the lanthanide ion is replaced by other ligands.

Introduction

The bands which occurred due to the low-lying 4f orbitals are few, sharp, and highly characteristic. This is due to electronic transitions (Laporte forbidden) within the f^n

configuration. It was postulated that the bands' intensity and shape would not be affected by ions complexing with the absorbing lanthanide ions since it was expected that only the outer (5d, 6s) valence shells would be influenced by such association. However, it is not so. The absorption spectra observed in simple aqueous solutions do change either in intensity or shape due to the formation of a complex. In this Spectro photometric study, a small change in the intensity of the absorption band is observed when the neodymium ion complexes with the nitrate anions. However, the change is sufficient for studying the changes in the near environment of the ions.

Several factors influence the formation of the lanthanide complexes. The nature of the lanthanide and the ligand are undoubtedly two of the most important ones, but the environmental factors like the temperature, and solvent are also significant. It is therefore of interest to see how solvent and temperature affect the interaction between the lanthanides and the ligands.
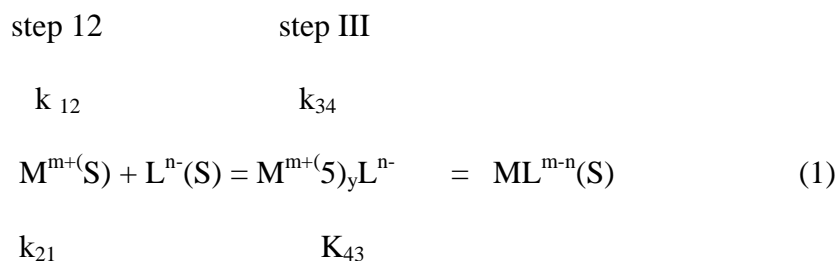
Studies on the effects of other organic solvents on the complexation of the lanthanide ions were first Initiated by Freed who had used spectroscopic methods to study the symmetry of lanthanide ions in solution, especially that around Eu(III) ions in ethanol and water. He found that the structures of the europium salts in ethanol are different from those in water. In recent years, there has been an emergence of various spectrophotometric techniques to investigate the complexation reactions. One of them is by Hamze and co-workers who have utilized a spectrophotometric method for the investigation of lanthanide halides in methanolic solutions to determine the effects of the solvent and solvation on the stability, electronic spectra, and structures of individual lanthanide complexes. Several thousand experimental optical density data covering all absorption ranges in the UV, visible and near IR were numerically treated. From this data, they discovered that the presence of water in the mixed methanol-water solvents leads to a decrease in the number and stabilities of the lanthanide chloro-complexes.

Silber and co-workers have studied the effects of methanol on the complexation 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.

Besides visible spectrocopy, Silber et al. have applied the ultrasonic relaxation technique as a spectroscopic and kinetic probe to examine the complexation of lanthanide nitrates in aqueous solutions.

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The use of this as a kinetic technique permits the separation of outer and inner sphere contributions, since lanthanide complexation follows a modified Eigen complexation mechanism.

$$
\begin{array}{ccc}
\text{step 12} & \text{step III} & \\
k_{12} & k_{34} & \\
M^{m+}(S) + L^{n-}(S) = M^{m+}(S)_y L^{n-} & = ML^{m-n}(S) & \quad (1) \\
k_{21} & K_{43} &
\end{array}
$$

where $M^{m+}(S)$ and $L^{n-}(S)$ represent solvated metal and ligand; $M^{m+}(S)yL^{n-}$ is an outer sphere solvent separated ion-pair, and $ML^{m-n}(S)$ is an inner sphere or contact ion pair formed by cation solvent loss combined with cation ligand bond formation.

Ultrasonic absorption measurements in water and aqueous organic solvents can differentiate between the two types of complexes, because step 12 is faster (occurs at higher frequency) than step III. if there are no inner sphere complexes in lanthanide systems, a small difference in sound absorption, α/f^2 (where f is the frequency) is observed between the salt solution and the solvent. When inner sphere complexes exist, a large difference is seen in the sound absorption between the test solution and the solvent. From the variation of absorption with frequency, it is usually possible to separate the data into both inner and outer sphere contributions.

Ultrasonic absorption measurements on $0.200M Nd(NO_3)_3$ solutions had been conducted in water and 50% methanol and the results were interpreted in terms of two forms of inner-sphere complexes which differ in solvation number. Since the ultrasound technique is unable to characterize the species in equilibrium, the present spectrophotometric study is necessary to better understand the system.

There have been several other spectrophotometric studies of the lanthanide nitrates in aqueous solutions. Using a differential spectrophotometric technique, Anagnostopoulos and Sakellaridis have studied these systems: $Pr^{3+}- NO_3^-$, $Sm^{3+} - NO_3^-$ and $Er^{3+}- NO_3^-$ in aqueous solutions. They found that $PrNO_3^{2+}$, $SmNO_3^{2+}$ and $ErNO_3^{2+}$ are the only complexes formed with absorption maxima at 444.2 nm, 403.8 nm and 378.0 nm, respectively.

In an attempt to unravel any possible systematic effects connected with inner-and outer sphere complex formation, the "hypersensitive" transition in $Nd^{3+}(aq)$ for $Nd(NO_3)_3$, $NdCl_3$ and $Nd(ClO_4)_3$ has been studied by Choppin, Henrie and Bui js[15]. By comparing the absorption spectra of the lanthanide ions with various ligands, It is found that in the case of the nitrates, the shape of the band is completely different. They explained that this is due to a

small concentration of the inner-sphere neodymium nitrate complex in equilibrium with a much larger concentration of the outer sphere complex. They also suggested that covalent effects are important for lanthanide complexes, since the ligands within each group share certain chemical and physical characteristics. Formation of covalent bonds between NO_3^- and Ln^{3+} ions has also been discovered by Katzin[16] who has investigated the spectra of $Pr(NO_3)_3$, $Nd(NO_3)_3$ and $Er(NO_3)_3$ solutions in tri-n-butyl phosphate.

Abrahamer and Marcus suggested that depending on the solvent and on the concentrations, both inner-and outer sphere nitrate complexes of the lanthanides are indeed formed in solution. From studies of the density and molar absorptivity of erbium nitrate solutions and the chemical shift of ,$^{17}O^-$ enriched water in the presence of Er and $LINO_3^-$, Er(III) was found to form inner sphere complexes with the nitrate ions. They deduced from the data that the nitrate ligand replaced water in the inner coordination sphere (hydration shell) of the Er(III) ion. Since the average ligand number in the Inner sphere is lower than the total ligand number, they proposed that some outer-sphere coordination also occurs for all the lanthanides in nitrate solutions.

Coward and Kiser have previously studied the complexation of Nd^{3+} and NO_3- ions in aqueous solutions using a differential spectrophotometric technique. Their results at 579 nm indicate that $Nd(NO_3)^{2+}$ is the only important absorbing species other than Nd^{3+}(aq) with an equilibrium constant of 0.77 at an ionic strength of 42. Foos, Kertes and Peleg have recorded the absorption spectra of neodymium in $LINO_3$–KNO_3 eutectic and its mixtures with water or chloride ions In the temperature range between $80 - 350°C$.18 They discovered that the molar absorptivity of some of the bands are sensitive to the environment.

Barinow and Tebleliew have studied the influence of HNO_3 concentration and some of its salts on the absorption spectrum of 0.05 M $Nd(NO_3)_3$ in water and found that both the mono and the bis-complexes are formed. Recently, Majdan and Sadowskl2have investigated the visible absorption of $Nd(NO_3)_3$ in a 90:10 methanol-water mixture. They found the

equilibrium constants to be $K_1 = 3.6$ and $K_2 = 1.0$ for $Nd(MeOH)_x NO_3^{2+}$ and $Nd(MeOH)_x(NO_3)_2^+$.

Using the stepwise equilibrium constants ratio as the basis for analysis, they found that these are inner sphere complexes. Although this study is similar to our work, the method that we proposed to use to calculate the equilibrium constants is quite different.

In our study, the program developed by Galzer was used to calculate the log of the equilibrium constants (log beta's). Recently, this program was modified and re-written In QBASIC which makes the calculation much faster. The existence of one or more complexes of the type MpLq with β defined as:

$$\beta = [MpLq] / [M]^P[L]^q \qquad ....(2)$$

is assumed In the Gaizer program. At each wavelength, Beer's Law is presumed to be valid, and that the deviation from Beer's Law is due to the formation of at least one complex. Therefore, the absorbance A is equal to the sums of the absorbances of each species, given by :

$$A = A_M + A_L + \sum_{1}^{p,q} A_{MpLq} \qquad (3)$$

If quartz cells with one cm pathlength are used in the spectral measurements; absorbance in the 1 cm cells becomes

$$A = \varepsilon_M[M] + \varepsilon_L[L] + \sum_{1}^{p,q} \varepsilon_{MpLq}[MpLq] \qquad (4)$$

Discussion

To use this program, the following data need to be entered; the total metal concentration [M], the total ligand concentration [L], the number of wavelengths used, and the absorbance of each solution at each wavelength, the number of complexes and first estimates of the logarithms of the overall complexation constant (β) and the molar extinction coefficients (E).

Initially, the program utilizes the first estimates at each wavelength independently to come up with the best set of molar extinction coefficients. It then uses the set of molar extinction coefficients and the concentrations of the free and complexed species to calculate the absorbances. Then, it applies the calculated data at all of the wavelengths to find the best equilibrium constants. The final values beginning with the inputs are then printed along with the square of the differences between the measured and the calculated absorbances (square of the residuals (U)). A new set of equilibrium constants is then entered and the process is repeated until a minimum value is found in the square of the residuals. This minimum value is found by plotting the log of equilibrium constants (log beta's) versus the square of the residuals. Theoretically, the result would be a V shaped curve, but in practice, a U-shaped curve is obtained. The best value of log beta is the minimum on the curve.
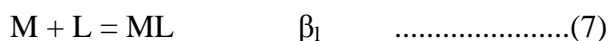
The In p, is related to the change in free energy (AG°) for the overall complexation process as

$$AG° = -RT \ln \beta_n \qquad ....(5)$$
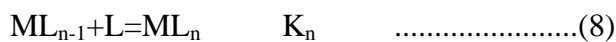
where β_n is the overall complexation constant. $\beta_n = K_1 K_2 .... K_n$ based on the following definitions for K (the stepwise equilibrium constant) andp:

$$M + L = ML \qquad K_l \qquad ....(6)$$

Pl is similar since

$$M + L = ML \qquad \beta_l \qquad ....(7)$$

but K_n and β_n differ because

$$ML_{n-1} + L = ML_n \qquad K_n \qquad ....(8)$$

whereas

$$M + nL = ML_n \quad \beta_n \qquad ....(9)$$

From these equations it is clear that $\beta_n = K_1 K_2 .... K_n.$

Since the Gaizer program calculates the results in terms of β_n, the results are first separated into K_n, the successive equilibrium constants- By determining each of these individual

equilibrium constants (K) as a function of temperature, it is possible to calculate $\Delta H°$ (the enthalpy of complexation) and $\Delta S°$ (the entropy of complexation) since :

$\Delta G° = \Delta H0 - T\Delta S°$ ....(10)

Combination of equation (10) with equation (5) gives equation (11)

In K = $-\Delta H°/RT + \Delta S°/R$ (11)

Thus, a plot of In K vs. 1/T would give a slope which is equal to $-\Delta H°/R$ and an intercept equals to $\Delta S°/R$.

Conclusion

The neodymium perchlorate and the neodymium nitrate stock solutions were made from the dried anhydrous oxide (Nd_2O_3) obtained from Molycorp Inc., by adding in the appropriate Inorganic acids. Distilled water was mixed in before dropping in the acid. While adding the acid, the mixture was also gently heated so as to hasten the reaction. The stock solutions were made either In water, or in methanol depending upon the kind of solvent composition needed. The high-water mole fraction stock solutions were made in water, and methanol was subsequently added.

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