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Acetohydroxamic Acid Complexes with Trivalent f-Block Metal Cations

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Acetohydroxamic acid has been studied by optical absorbance spectroscopy as a complex forming reagent for the lighter trivalent lanthanides and actinides (Pu(III) and Am(III)) in aqueous solution at 2.0 M ($NaClO_4$) ionic strength. The highest stoichiomery in all the cases studied has been found to be a 1:4 metal-to-ligand ratio; formation of tetrahydroxamato species requires a high excess of the ligand and alkaline pH. Spectrophotometric monitoring confirmed the presence of Pu(III) by electrochemical reduction of Pu(IV) in the course of the pH titration experiment. The formation constants can be used for optimization of processing flowsheets in the advanced PUREX process

Keywords: Acetohydroxamic acid, lanthanides, Pu(III), Am(III), spectrophotometry, formation constants

I. Introduction

Acetohydroxamic acid (AHA) has received increasing attention as a complexing agent capable of selective stripping of Np(IV) from U(VI) when both actinides are present in the solvent stream of the advanced PUREX process [1)]. No formation constants have been reported for An(III) and An(IV) complexes with AHA although stability constant for some lanthanides determined by potentiometric titration at 0.1 M ionic strength have been reported [2)]. In the present study, optical absorbance spectroscopy has been used to measure the stability constants of AHA with the lighter lanthanides (Ce to Gd) and Pu(III) and Am(III). In these measurements spectrophoto-metric monitoring was used in the complexation experiments involving redox sensitive cations (Ce(III) and Pu(III). The method also allowed observation of charge transfer effects in Eu(III)-AHA complexes. The stability constants found show both similarities and differences between the Ln(III) and An(III) metal cations.

II. Experimental

1. pH measurement

A micro pH electrode (Corning, G-P Micro Combo) connected to an Accumet 950 pH/ion meter was used to control the pH of solutions in the course of the spectrophotometric titration experiments. The pH meter was calibrated using standard buffer solutions of pH 4.00 and 10.00 (Fisher Scientific)

2. Preparation and standardization of Ln(III) and An(III) solutions

Ln(III) stock solutions were prepared by dissolution of the corresponding oxides (better than 99.9% purity) in an appropriate amount of perchloric acid. Standardization of stock solutions was performed by complexometric titration with EDTA using Xylenol Orange as an indicator. Trivalent actinide concentrations were determined in working solutions by measuring the optical densities of their major peaks using molar absorptivities from the literature.

3. Spectrophotometric titration

An OLIS upgraded Cary-14 spectrophotometer was used for acquisition of optical absorbance spectra in the course of alkaline titration of metal-ligand solutions by solutions of carbonate-free NaOH. The metal concentration was selected to be sufficient for reliable detection of its optical absorbance with the signal-to-noise ratio typically not less than 30 ($A > 0.03$). If the cation absorbance bands were very weak (Gd), a 100 mm cylindrical cell was used to keep metal concentration as low as possible for the reliable spectrophotometric detection. In most cases the ligand was used in a significantly higher molar excess with respect to the metal cation than is normally used in potentiometric titrations. This was done to suppress formation of hydroxy and carbonato complexes of the metal under study to submicromolar concentrations, i.e. to make such species negligible with respect to concentrations of hydroxamate complexes of the metal. High excess of the ligand also allowed better observation of spectral features of tetrahydroxamate complexes whose existence had not been reported in the literature.

4. Electrochemically controlled Pu(III)-AHA complexation experiment

A five neck conical electrochemical cell (N_2 purged) was employed to produce pure solutions of Pu(III) by reduction of tetravalent plutonium in 1M $HClO_4$/1M $NaClO_4$ solution (total volume of Pu solution was 4 mL). All additions of NaOH to shift the pH of the Pu(III) + AHA solutions to higher values were done directly into the cell with immediate readjustment of the working electrode potential to more negative values to keep it slightly above the hydrogen liberation potential of the solution at a given pH. The solution portion for spectrophometric detection (~ 1ml) was then withdrawn and placed in a nitrogen flushed cuvette. After completion of each spectral acquisition (~ 3 min), it was noticed that the upper portion of the solution in the cuvette (~200-300 mcL) had changed its color from sky-blue to orange-brown, presumably as a result of ambient air penetration into the cuvette space above the solution and oxidation of Pu(III) to Pu(IV). Fortunately, the light beam propagation spot was located below the oxidized layer and, in most cases, not less than 98% of Pu was preserved in

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trivalent state in the detection zone. The cuvette content was returned to the main portion of Pu(III)-AHA solution with electrochemical reduction of the oxidized portion of Pu to the trivalent state. A decreased electric current indicated that the valence purity of Pu(III) had been restored. The experiment then proceeded to the next addition of NaOH solution step. The solution aliquot for spectrophotometry was not withdrawn until the solution was electrolyzed to eliminate any additional Pu(IV) formed.

5. Data processing

a) Species Analysis. The Singular Value Decomposition (SVD) was used for estimation of a number of spectrophotometrically distinct species in optical absorbance spectra data set without any a priori assumptions of chemical nature (the validity of the Beer law is, however, required) [3]. The SVD has been extensively used throughout this project to substantiate a choice of chemical model for the subsequent data analysis.

b) Formation constants A modified version of the SQUAD code [4] was employed to refine the stability constants obtained from the spectrophotometric data.

III. Results and discussion

1. Protonation constant of acetohydroxamic acid at 2.0 M ionic strength

The pK_a of acetohydroxamic acid was determined by alkaline titration of a 10 mM solution in combination with spectrophometric detection of optical absorbance of the conjugate base in the UV spectrum (255-270 nm wavelength range) at different pH values. The spectral data was processed by SQUAD and a pK_a of 9.018 (0.003) obtained for the protonation constant of AHA.

2. Trivalent lanthanides

Six Ln(III) metal ions, which possess light absorbing properties in solution, were chosen for examination of their complexation behavior by UV-Vis spectroscopy. When possible, the scanning range was selected to be wide enough to incorporate at least two non-overlapping absorption peaks. This allowed analysis of two data sets from each experiment by processing each peak region separately, followed by averaging of the two sets of stability constants. This approach made it possible to obtain more reliable values of uncertainties with simultaneous reduction of systematic errors due to possible drifts of the instrumental baseline over time. In the case of Ce(III), where a single peak was available for data collection, the experiments were repeated several times with different metal-to-ligand ratios to obtain average values of the corresponding stability constants.

As a typical example of two data sets in one experiment **Fig.1** shows the spectral changes for Nd(III) in the presence of AHA while maintaining the total ligand to total metal ratio constant and with progressive elevation of pH to increase the free ligand concentration. Subsequently, the entire spectral range examined was split onto two regions: the first extended from 510 to 540 nm and included 121 data points; the second was centered around the hypersensitive peak of Nd(III) at 576 nm and had 141 points. The spectral data sets showed good convergence to the best estimates of the stability constants providing that, in the absence of appreciable baseline drifts, the refined values agreed well.

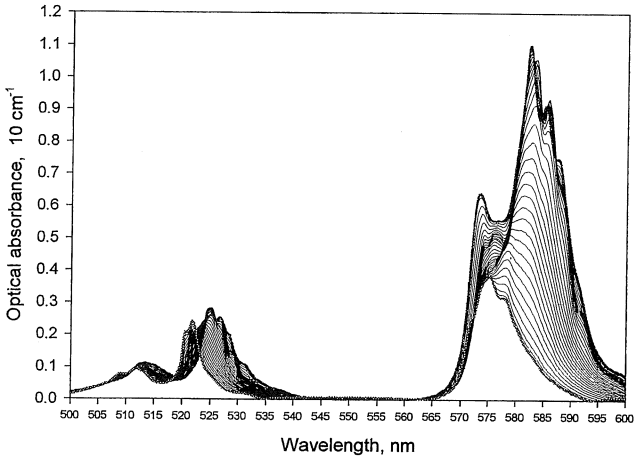

Fig.1 Optical absorbance spectra of Nd(III) in the presence of AHA at different pH. C_{Nd} = 5.6 mM, C_{AHA} = 370 mM, pH range from 2.01 to 9.60; 20°C; I = 2.0 M ($NaClO_4$)

Molar absorptivities of the separate $NdAHA_n$ species for which spectral shapes and intensities contain valuable information about symmetry and other structural aspects of the coordination environment of the metal and ligand for each stoichiometry are be presented in a subsequent publication, along with data for other light absorbing lanthanides. Eu(III) is the most interesting lanthanide for probing its complexation behavior with AHA spectrophotometrically, because its spectra show effects of both hypersensitivity (a narrow and extremely weak peak at 465 nm) and a broad and intense charge transfer band in the UV part of spectrum with an absorbance well above 400 nm, resulting in the yellow coloration of the solution (especially in weakly acidic solutions). **Table 1** lists the formation constants for the lanthanides studied.

Analysis of the formation constants of lanthanide monohydroxamates as a function of the reciprocal of the ionic radius of the metal cation shows that this dependence is a linear function for the four consecutive lanthanides: Pr, Nd, Sm and Eu. However, Ce(III) and Gd(III) appear to be notable exceptions to this trend, because their K_1 values are 0.3 log units lower than the values predicted by extrapolation of the Pr-Nd-Sm-Eu data. Such a negative deviation from the linear trend has been extensively reported for Gd [5] (the "gadolinium break"), but such a deviation for Ce(III) is unusual. The Ce(III) experiments were repeated three times with more efficient elimination of dissolved and gaseous oxygen from the reaction container. The third attempt made it possible to exclude any significant amount of $Ce(IV)AHA_n$ complexes. The preservation of Ce(III) valence required more rigorous precautions than normal in potentiometric experiments. Thus, our studies indicate the need for caution in assessing the validity of Ce(III) complexation with strongly complexing ligands as the presence of Ce(IV) can produce positively biased values of formation constants.

Table 1. Formation constants of lighter lanthanides with acetohydroxamic acid. Temperature 22 ± 1 °C, I = 2.0 M ($NaClO_4$). Values in brackets represent standard deviations of formation constants refined from different absorption peaks data sets. Values in square brackets show literature values[2] for 0.1 M ionic strength ($NaNO_3$).

Ln(III)	Ce	Pr	Nd	Sm	Eu	Gd
Ionic radius, pm [6] (CN=6)	101.0	99.0	98.3	95.8	94.7	93.8
Spectral range, nm	280-350	430-500	500-600	390-415	462-468	303-315
$\log\beta_1$	5.08 (0.02)	5.69 (0.08)	5.72 (0.02)	6.02 (0.05)	6.19 (0.06)	5.96 (0.03)
$\log\beta_2$	9.47 (0.03)	10.81 (0.05)	10.98 (0.01)	11.68 (0.10)	11.97 (0.10)	11.65 (0.07)
$\log\beta_3$	13.05 9.03)	14.31 (0.15)	14.56 (0.03)	15.29 (0.15)	15.85 (0.26)	15.40 (0.40)
$\log\beta_4$	13.75 (0.04)	14.99 (0.20)	14.94 (0.11)	16.26 (0.02)	17.32 (0.15)	16.86 (0.36)
$\log K_1$	5.08 [5.45]	5.69	5.72	6.02 [5.96]	6.19	5.96 [6.10]
$\log K_2$	4.39 [4.34]	5.12	5.26	5.66 [4.77]	5.78	5.69 [4.76]
$\log K_3$	3.58 [3.01]	3.50	3.58	3.61 [3.68]	3.88	3.75 [3.07]
$\log K_4$	0.70	0.68	0.38	0.97	1.47	1.46

3. Trivalent actinides

(1) Am(III)

Much higher molar absorptivity of trivalent americium compared with that of 4f-metals in solution allowed complexation experiments at submillimolar concentration of the Am(III). Spectra acquired in the course of the spectrophotometric titration are shown in **Fig.2**. Molar absorptivities of separate complexed species ($AmAHA_n$) along with analysis of the number of species indicated the consecutive appearance of four specrophotometrically distinct species in solution (presumably of 1:1, 1:2, 1:3 and 1:4 stoichiometry).

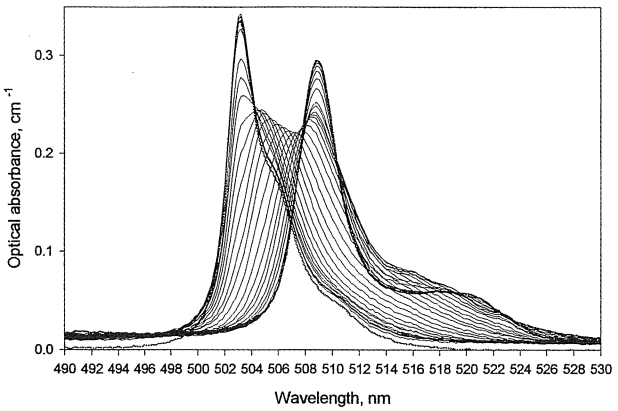

Fig.2 Spectrophotometric monitoring of complexation effects between Am(III) and AHA. C_{Am} = 0.85 mM; C_{AHA} = 88 mM; pH range 0.52 –10.01

(2) Pu(III)

As for Ce(III), measurements with trivalent plutonium required special precautions to keep the cation in its trivalent oxidation state in solution (see experimental section for more details). In total, 30 spectra were collected in the pH range 0.01 to 9.59 with the ligand-to-metal ratio of 22:1. The hydrolysis constants of Pu(III) available in literature show much higher acidity of its hydrated cation compared with Ln(III) analogues and Am(III)[7]. The ligand was introduced at pH ~ 0 and the first 10 –12 pH increments were done in small steps. This was done to detect spectral differences if complexation started at higher acidity than usual with the more 'predictable' 4f-metal ions and Am(III). In fact, no noticeable spectral changes were observed until the pH reached to 3.43 (for Ln(III),this happened in the pH range from 2.8-3.0 for Eu(III) and Gd(III) and 4.0-4.2 for Ce(III)). This observation, qualitatively, indicated that Pu(III) behaves similarly to its analogues in the starting phase of complex formation with AHA. The spectral preprocessing revealed that the mixture of $Pu(IV)AHA_m$ complexes in the total Pu(III) balance did not exceed 2% for 28 of 30 spectra collected and, in those two cases, it amounted to ~4%. Consequently, these two spectra were discarded and, after appropriate spectral correction to eliminate contribution from tetravalent Pu, the spectral set was processed by SQUAD. **Fig.3** shows the corrected spectra.

4. Comparison of formation constants for Am(III) and Pu(III)

Analysis of the corresponding stability constants for americium and plutonium hydroxamates (**Table 2**) shows both similarities and differences with the respective values for the Ln(III) isoelectric and size analogues.

The first formation constants for Pu(III) and Am(III) differ by less than 0.1 log units and their magnitudes place them in positions close to Pr(III) and Nd(III), respectively, rather than to Sm(III) and Eu(III), the isolectronic counterparts. It is noteworthy that the $\log K_1^{(Pr)}$ - $\log K_1^{(Nd)}$ difference is even smaller than that of Pu(III) and Am(III). In the case of lanthanides this was a subject of active discussion in the middle 60's as a manifestation of the first phase of the so-called tetrad effect.

The second (stepwise) formation constant for the 5f elements examined differ from each other by almost 0.6 log units. The $\log K_2^{(Pu)}$ value causes this difference, as the Am(III) value is close to its expected position between Nd(III) and Pm(III) in the ionic radius scale.

The difference between $\log K_3^{(Pu)}$ and $\log K_3^{(Am)}$ is even larger (>1 log unit); not only does Pu(III) deviate from the interpolated 4f-metal series value between Ce(III) and Pr(III)

but $\log K_3^{(Am)}$ also does not fit its expected position between Nd(III) and Pm(III).

The complex formation for $An(AHA)_4$ is characterized by fairly similar values for $\log K_4^{(Pu)}$ and $\log K_a^{(Am)}$ (0.10 log

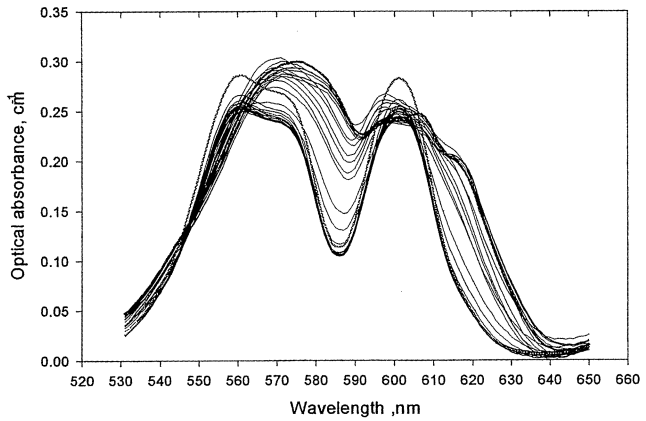

Fig.3. Pu(III) spectra in the presence of AHA after correction for optical interference from Pu(IV) complexes. C_{Pu} = 8 mM, C_{AHA} = 165 mM, pH range: 0.01 – 9.59

Table 2. Stability constants of Pu(III) and Am(III) with acetohydroxamic acid (22± 1°C; I=2.0 M ($NaClO_4$)

An(III)	Pu(III)	Am(III)
$\log\beta_1$	5.77 (0.05)	5.85 (0.01)
$\log\beta_2$	11.66 (0.04)	11.17 (0.01)
$\log\beta_3$	14.84 (0.06)	15.48 (0.01)
$\log\beta_4$	15.85 (0.11)	16.59 (0.03)
$\log K_1$	5.77 (0.05)	5.85 (0.01)
$\log K_2$	5.89	5.32
$\log K_3$	3.18	4.31
$\log K_4$	1.01	1.11

difference), with both values being 0.3-0.4 units higher when compared with the Pr(III)-Nd(III) couple.

In general, tetrahydroxamates of Pu(III) and Am(III) are about 1.3 and 1.2 log units higher than their Ln(III) ionic radii analogues which bring Pu(III) and Am(III) overall complexation strengths closer to Sm(III), 0.4 log units lower and 0.35 log units higher than $\log\beta_4^{(Sm)}$, respectively.

Further experiments with Pu(III) are needed with some experiment in order to judge more definitely whether the observed jumps in the $\log K_2$ and $\log K_3$ values versus the respective values for Am(III) come from inherent complexation chemistry of this most chemically diverse element in the actinide series or if they are the result of some perturbation due to some Pu(IV) in the solutions.

IV. Conclusion

Spectrophotometry has proven to be an efficient technique for quantitatively measuring subtle differences in complexation behavior, providing valuable information about ligand-metal structural environment in the $Ln(III)AHA_n$ complexes. Pu(III) and Am(III) show both similarities ($\log K_1$) and differences in comparison with their Ln(III) analogs of closest ionic radii. Examination of Np(III) and Cm(III) complexation with acetohydroxamic acid would contribute to a better understanding of these differences. Extension of the An(III) list to four consecutive members of the series would also help to understand spectroscopic features of $An(III)AHA_n$ species in comparison with the corresponding isoelectronic Ln(III) cations and to examine effects of hypersensitivity in the An(III) complexes.

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