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HIGH-TEMPERATURE SPECTROSCOPY FOR NUCLEAR WASTE APPLICATIONS

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Instrumentation has been developed to perform uv-vis-nir absorbance measurements remotely and at elevated temperatures and pressures. Fiber-optic spectroscopy permits the interrogation of radioactive species within a glovebox enclosure at temperatures ranging from ambient to $>100^{\circ}\text{C}$. Spectral shifts as a function of metal-ligand coordination are used to compute thermodynamic free energies of reaction by matrix regression analysis. Pr^{3+} serves as a convenient analog for trivalent actinides without attendant radioactivity hazards, and recent results obtained from 20° - 95°C with the Pr-acetate complexation system are presented. Preliminary experimentation on Am(III) hydrolysis is also described.

INTRODUCTION

The present strategy for the underground burial of high-level nuclear wastes in a geologic repository depends upon safeguards against radionuclide migration into the biosphere for up to 10,000 years after site closure.¹ This large extrapolation in time requires that geochemical modeling play a central role in the assessment of waste isolation, and theoretical efforts for this purpose are active areas of current research.²

Modeling software requires thermodynamic data relevant to interactions of actinides and other radioisotopes with groundwater and various geologic media. Although much data exist³ for chemical interactions around 25°C , the same is not true for systems at the elevated temperatures expected in the near-field vicinity of a nuclear repository. Knowledge of important reaction parameters of aqueous

systems in the 50 - 150°C regime is imperative for reliable prediction of potential waste migration under pragmatic scenarios. Although calculations based on lower-temperature data can be used to estimate high-temperature thermochemical properties,⁴ experimental measurement of equilibrium constants and enthalpies at elevated temperatures should provide more accurate data for input to modeling codes.

We have developed apparatus to perform optical spectroscopy at 20 - 125°C within the regulated enclosure of a radioactivity glovebox. Measurements are effected remotely with fiber-optic probes, and sample temperature is regulated with a dry-block heater. Metal-ligand stability constants (free energies of reaction) can be computed from changes in wavelength and absorbance as the degree of metal complexation is varied.⁵

We report stability-constant measurements for the praseodymium-acetate (Pr-ac) system at temperatures of 20, 50, 65, 80, and 95°C. The Pr^{3+} cation is a useful analog for trivalent actinide species without the accompanying radiation hazard.⁶ Initial experimentation on Am^{3+} hydrolysis was also performed with the high-temperature spectroscopy (HiT-SPEC) instrumentation.

EXPERIMENTAL

For the Pr-ac experiments, solutions with varying ligand-to-metal (L/M) ratios were synthesized from Pr_6O_{11} , acetic acid, and HClO_4 . The inert salt NaClO_4 was used to adjust each individual solution to a total ionic strength $I = 1.00$ M. All reagents were of analytical reagent-grade quality or better, and details of solution preparation and characterization are presented elsewhere.⁷ The Pr-ac solutions had compositions of approximately $[\text{Pr}]_t = 19$ mM, $0 \leq [\text{ac}]_t \leq 400$ mM, $\text{p}[\text{H}] = 4.4 - 4.7$, and $I = 1.00$ M (NaClO_4). The solutions for the study of Am(III) hydrolysis were $[^{243}\text{Am}] = 10^{-4}$ M, $\text{p}[\text{H}] = 4.8 - 6.7$, and $I = 0.50$ M (NaClO_4).

The core of the HiT-SPEC instrumentation is a Guided Wave model 200 fiber-optic spectrometer.^{8,9} Absorption measurements on the Pr-ac solutions were made over 415 - 515 nm in 0.05-nm intervals, and between 490 - 530 nm ($\times 0.05$ nm) for the Am(III)-hydrolysis experiments. Temperature regulation of a solution was

effected with a modified Techne model DB-1 Dri-Block heater, and, for the Pr-ac absorbance data, setpoints of $t = (20 \pm 0.6), (50 \pm 0.5), (65 \pm 0.5), (80 \pm 0.6),$ and $(95 \pm 0.5)^\circ\text{C}$ were maintained. A thorough description of the instrumentation and spectral data-acquisition procedure can be found elsewhere.¹⁰

DATA ANALYSIS

Guided Wave data files were processed on an IBM PS/2. Spectra Calc software (Galactic Industries Corp.) was used for background subtraction and baseline normalization. For the Pr-ac experiments, data spanning the $\text{Pr}^{3+} \text{}^3\text{H}_4 \rightarrow \text{}^3\text{P}_0$ transition at 482 nm were analyzed by the program SQUAD¹¹ for each studied temperature; for Am(III)-hydrolysis, the absorption peak at 503 nm was utilized.

SQUAD employs matrix regression analysis to calculate multiparameter values (overall formation constants β_i and corresponding extinction coefficients $\epsilon_{i,\lambda}$ at each input λ) by solving mass-balance equations and fitting the measured absorbance data. In the present Pr-ac experimental system, two metal-ligand complexes and one acid species have been previously observed at 25°C .³ For each individual analytic solution, therefore, the total metal concentration, M_t , is given by¹²

$$M_t = \sum_{i=0}^2 [ML_i] = [M](1 + \sum_{i=1}^2 \beta_{10i}[L]^i) \quad (1)$$

Similarly, the total acetate concentration, L_t , is expressed by

$$\begin{aligned} L_t &= \sum_{j=0}^1 [H_j L] + \sum_{i=0}^2 i [ML_i] \\ &= [L](1 + \beta_{011}[H^+]) + M_t \cdot \left(\frac{\sum_{i=1}^2 i \beta_{10i}[L]^i}{1 + \sum_{i=1}^2 \beta_{10i}[L]^i} \right) \\ &= [L](1 + \beta_{011}[H^+]) + M_t \cdot \bar{n}_L \end{aligned} \quad (2)$$

where β_{011} is the protonation constant of acetic acid and $\bar{n}_L$ is the average ligand number. [The subscript triple-indices refer to the number of atoms of metal, hydrogen, and ligand, respectively, in the complex. Thus, "0i1" indicates the

reaction $iH + L \rightleftharpoons H_iL$, "10j" indicates $M + jL \rightleftharpoons ML_j$, etc.] The measured total absorption at a given λ , $A_{t,\lambda}$, is described by Beer's Law

$$A_{t,\lambda} = l \sum_{i=0}^2 \epsilon_{(\lambda,i)} [ML_i] \quad (3)$$

where l is the optical path length.

SQUAD arrives at a final result through an iterative procedure that entails initial estimates of the β_i . It first calculates free-ligand concentration $[L]$ and then all other species concentrations $[ML_i]$. With these data, a linear regression fit to $A_{t,\lambda}$ in equation (3) gives best values of all of the extinction coefficients at a chosen λ . A calculated total absorbance, $A_{t,calc}$, is then compared with the measured value to compute an unweighted sum-of-squares. The full comparison is actually a double summation over all solutions, x , and over all incorporated wavelengths, λ :

$$U^2 = \sum_{\lambda} (\sum_x [A_{t,calc} - A_{t,exper.}]^2) \quad (4)$$

This computation is then repeated with new values of β_i until U^2 is minimized and the convergence criterion is satisfied.

Only the metal stability constants were permitted variation in these analyses. Acid constants were fixed at values determined by interpolation of high-temperature potentiometric data measured by MESMER *et al.*¹³ As discussed in detail elsewhere,¹⁰ the measurement of $p[H]$ at elevated temperatures was avoided by treating the total hydrogen inventory (H_t) of each solution as a conserved quantity and allowing $[H^+]$ to vary as a free parameter, analogous to a second metal species in solution.

RESULTS AND DISCUSSION

In the Pr-ac experiments, at any given temperature the absorption spectra displayed increasing redshift with increasing L/M . This behaviour has been previously observed in other studies with Pr at room temperature.^{7,14} For the Am(III)-OH series, increasing hydrolysis was manifest as decreasing absorbance in the 503-nm peak.

Experimental results for the first two Pr-ac stability constants are presented in Table 1, and these data are corrected for the thermal expansivity of aqueous solutions. All equilibrium-constant uncertainties listed in this work are 1σ values and are the errors reported by SQUAD.¹¹ They are thus minimum values associated with this work, as no attempt was made to propagate uncertainties inherent in solution syntheses, p[H] assays, etc. However, the latter errors are unquestionably small compared to those inherent in the optical data and regression analyses.

Table 1. Overall stability constants at $I = 1.0\text{ M}$ for the system: $\text{PrL}_{i-1} + \text{L} \rightleftharpoons \text{PrL}_i$ for $i = 1-2$ and $\text{L} = \text{acetate}$.		
$t(^{\circ}\text{C})$	β_{101}	β_{102}
20	63 ± 4	350 ± 50
50	54 ± 6	330 ± 70
65	47 ± 5	490 ± 90
80	57 ± 7	610 ± 100
95	62 ± 4	300 ± 50

Comparison of the results of this work at 20°C with 25°C -data measured by potentiometry,^{7,15} visible spectroscopy,⁷ and laser-induced photoacoustic spectroscopy⁷ is possible. The Pr-ac HiT-SPEC results for both β_{101} and β_{102} are in very good agreement with the existing literature.

The Am(III)-hydrolysis investigation was hindered by a lack of p[H] control. The p[H] stability of several of the analytic solutions was but marginally acceptable,

and the results of this study can only be considered preliminary or semi-quantitative at best. Nevertheless, the SQUAD result for the first hydrolysis constant at 22°C was $\log K_{1-10} = -7.5 \pm 0.6$. The expected value computed from NEA-selected data and Specific-Ion Interaction Theory is -7.12 at $I = 0.5 \text{ M}$.¹⁶ These experiments will be repeated with suitably-buffered Am(III) solutions in the near future.

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