Conf- 910422--5

UCRL-JC-106028
PREPRINT

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This paper was prepared for the
Methods and Applications of Radioanalytical Chemistry II
Kona, HI
April 21-27, 1991

Manuscript Date: September 1991
Publication Date: October 1991

Lawrence Livermore National Laboratory

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HIGH-TEMPERATURE SPECTROSCOPY FOR NUCLEAR WASTE APPLICATIONS

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UCRL-JC--106028

DE92 002167

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°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 exist[3] 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 $[Pr]_t$ = 19 mM, 0 ≤ $[ac]_t$ ≤ 400 mM, p[H] = 4.4 - 4.7, and I = 1.00 M ($NaClO_4$). The solutions for the study of Am(III) hydrolysis were $[^{243}Am] = 10^{-4}$ M, p[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 (× 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 ± 0.6), (50 ± 0.5), (65 ± 0.5), (80 ± 0.6), and (95 ± 0.5)°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 Pr^{3+} $^3H_4 \rightarrow {}^3P_0$ transition at 482 nm were analyzed by the program SQUAD[11] 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 $\varepsilon_{i,\lambda}$ 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 by[12]

$$M_t = \sum_{l=0}^{2} [ML_l] = [M](1 + \sum_{l=1}^{2} \beta_{10l}[L]^l) \qquad (1)$$

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

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

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

$$A_{t,\lambda} = l\sum_{l=0}^{2} e_{(\lambda,l)}[ML_l] \qquad (3)$$

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_l]. 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:

$$U^2 = \Sigma_\lambda(\Sigma_x[A_{t,calc.} - A_{t,exper.}]^2) \qquad (4)$$

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 M
for the system: $PrL_{i-1} + L \rightleftharpoons PrL_i$
for i = 1-2 and L = acetate.

t(°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 spectroscopy[7] 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 M.[16] These experiments will be repeated with suitably-buffered Am(III) solutions in the near future.

ACKNOWLEDGEMENTS

Prepared by Yucca Mountain Site-Characterization Project (YMP) participants as part of the Civilian Radioactive Waste Management Program. The YMP is managed by the Yucca Mountain Site-Characterization Project Office of the U.S. Department of Energy, Las Vegas, Nevada.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

This paper is dedicated to the memory of Dr. D.F. Patrick Grant for a lifetime of devoted service to family and community health care.

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01/07/92