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DEVELOPMENT OF HIGH-TEMPERATURE UV-VIS-NIR SPECTROSCOPY
FOR THE MEASUREMENT OF FREE ENERGIES OF COMPLEXATION
AT ELEVATED TEMPERATURES

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ABSTRACT

We have developed instrumentation capable of measuring optical absorption spectra over a wavelength range of 200-1200 nm and a temperature range of 20-100°C. This fiber-optic based spectrometer generates data which allow the computation of metal-ligand equilibrium constants. Studies at five temperatures have been completed using praseodymium-diglycolate as a model system. Fundamental thermodynamic values (free energies, enthalpies, entropies) were obtained from the experimentally-determined stability constants.

INTRODUCTION

Thermodynamic data pertinent to the interactions of actinides and long-lived fission products with groundwater, waste package components, and geologic media are critical input to modeling programs. While numerous measurements exist for systems at classical thermodynamic temperatures near 25°C, [1] the near-field environment of a nuclear repository will experience elevated temperatures ensuing from radiation heating and normal ambient subsurface temperature. [2] Although 25° data are often used for modeling efforts to predict chemical behavior at higher temperatures, the results of these computations are necessarily more uncertain with this approximation. Empirical measurements of free energies and enthalpies at high temperature should provide a more reliable and accurate database for implementation by modeling codes.

We have developed instrumentation capable of uv-vis-nir spectroscopy at elevated temperature while contained in the regulated enclosure of a high-level radioactivity glovebox. Spectroscopic measurements are performed remotely with fiber-optic probes, and temperature control of the sample is maintained by a dry-block heater. We chose praseodymium-diglycolate (Pr-digly) as the initial chemical system for study. From small shifts in wavelength and optical absorption as a function of complexation, metal-ligand stability constants (free energies of reaction) can be calculated under suitable experimental conditions. [3]

We report stability-constant measurements for the Pr-digly complexes at temperatures of 23, 50, 65, 80, and 95°C. The Pr-digly system does not have any direct relevance in modeling the environment of a nuclear repository, but some comparison of the present variable-temperature results with conventional techniques [4,5] was possible as a primary "proof-of-principle."

MASTER

EXPERIMENTAL

Reagents

Analytical solutions of varying ligand-to-metal (L/M) ratios were prepared from reagent Pr_2O_3 [$>99.9\%$, Alfa], diglycolic (oxydiacetic) acid [$>99\%$, Aldrich], and HClO_4 . Reagent-grade NaClO_4 [G.F. Smith] was utilized to adjust each solution to a total ionic strength $I = 1.00 \text{ M}$. Details of solution preparation and measurements of metal and free-acid concentrations ($p[\text{H}]$) are given elsewhere.[5]

Spectroscopic measurements were made on 13 Pr-digly solutions. The compositions of these solutions (total concentrations) were: $[\text{Pr}]_t = 19.3 \text{ mM}$, $0 \leq [\text{digly}]_t \leq 79.5 \text{ mM}$, $p[\text{H}] = 3.73\text{--}4.13$, and $I = 1.00 \text{ M}$ (NaClO_4).

Methodology

The nucleus of the instrumentation is a Guided Wave Model 200 fiber-optic spectrophotometer.[6,7] The unit is capable of single-beam scanning over the wavelength range $\lambda = 200\text{--}1200 \text{ nm}$, and two 7-fiber bundle probes transport spectrometer light to and from a glovebox enclosure over 2-meter lengths of optical cable. Overall system resolution is nominally $\sim 1 \text{ nm}$. Calibration measurements with NIST primary-standard wavelength filters confirmed that spectrometer performance was at least 1 nm from $\lambda = 440\text{--}740 \text{ nm}$.

Temperature control of an experimental solution was maintained with a modified Techne model DB-1 Dri-Block heater. The actual temperature of the solution during spectral data acquisition was measured with a teflon-coated thermocouple and display meter (Omega). For the present experiments, Pr-digly absorption data were obtained at $t = (23 \pm 1)$, (50 ± 0.6) , (65 ± 0.5) , (80 ± 0.6) , and $(95 \pm 0.5)^\circ\text{C}$. An overpressure of reagent nitrogen was maintained during all high-temperature experiments to regulate the vapor pressure of water approximately equivalent to that at 25°C ; maximum overpressure for the present work (at 95°C) was about 180 kPa . The acquisition of optical absorption data, as well as instrumental control of the spectrometer, were performed by means of commercial Guided Wave software running on an IBM XT personal computer.

After a Pr-digly solution was introduced into a quartz optical cell, the unit was closed to the environment. Temperature and pressure settings were adjusted, and the solution was allowed to equilibrate for one hour. Absorbance measurements between $415\text{--}515 \text{ nm}$ were then recorded in 0.05-nm intervals. Normalization of all Pr-digly spectra to a He-Ne 632.8-nm primary calibration filter was made. Scans of the filter were made immediately before and after each solution spectrum, and this normalization procedure successfully corrected for monochromator drift of the spectrometer, which was found to approach 0.5 nm or more during a system operation of six hours. Adjustment and equilibration of that same solution to the next higher temperature and pressure followed next, with the cycle repeated at each desired temperature.

Data Analysis

The Guided Wave data file was imported into Spectra Calc (Galactic Industries Corp.) for processing on an IBM PS/2. Baseline normalization of each spectrum was accomplished by subtracting a background determined by a linear fit of data in the zero-absorption regions neighboring 415 and 515 nm. All spectral data at a given temperature and a λ range of 480-488 nm were then prepared for input to the analysis program SQUAD.[8] SQUAD computes values of stability constants and extinction coefficients by a matrix regression technique.

For these analyses, only the metal stability constants were allowed to vary, and the acid constants were fixed at values obtained from the work of Grenthe and Ots.[4] They measured $\log \beta_{011}$, $i = 1, 2$, over the range 5-65°C. We found these data to be reasonably described by a linear function of $\log \beta$ vs t for both acid species. We therefore extrapolated these functions to obtain values of the two acid constants at $t = 80$ and 95°C .

Another aspect of the SQUAD computations that required novel consideration was the treatment of solution $p[H]$ at high temperatures. The total hydrogen inventory of a solution, H_t , was assumed constant at all temperatures (similar to the inventories of M_t and L_t). Known acid constants, experimental $p[H]$ values, and measured metal stability constants at 25°C were therefore used to calculate H_t .

Figure 1. Variation of peak position and intensity with L/M at constant temperature (50°C) for the Pr-digly system. Increasing L/M increases spectrum redshift and decreases peak absorption.

RESULTS AND DISCUSSION

At any given temperature, as previously observed by other investigators at room temperature,[9] the absorption spectra exhibited increasing redshift with an increase in metal complexation (Figure 1). In the Pr-digly experimental system, three metal-ligand complexes $[\text{Pr}(\text{digly})_i]^{3-2i}$ with $i = 1-3$ and two acid species $[\text{H}_j(\text{digly})]^{j-2}$ with $j = 1,2$ have been previously observed at 25°C.[1,4] The stepwise stability constants measured for the Pr-digly system by the present technique are given in Table I. Reliable values of the first constant were not obtained at 50° or 95°, a likely consequence of the limited spectrometer resolution adversely affecting those data sets at the very small redshifts characteristic of the first complex.

Table I. Experimental results of stepwise stability constants at $i = 1.0 \text{ M}$ for the system: $\text{PrL}_{i-1} + \text{L} \rightleftharpoons \text{PrL}_i$ for $i = 1-3$ and $\text{L} = \text{diglycolate}$.

$t(^{\circ}\text{C})$	K_{101}	K_{102}	K_{103}
23	$(2.1 \pm 0.6) \times 10^5$	$(5.0 \pm 2) \times 10^3$	$(5.8 \pm 3) \times 10^2$
50	-	$(7.1 \pm 2) \times 10^3$	$(4.7 \pm 2) \times 10^2$
65	$(1.5 \pm 0.9) \times 10^5$	$(6.0 \pm 6) \times 10^3$	$(3.0 \pm 4) \times 10^2$
80	$(3.2 \pm 1) \times 10^5$	$(4.9 \pm 4) \times 10^3$	$(8.9 \pm 7) \times 10^1$
95	-	$(1.2 \pm 0.7) \times 10^4$	$(5.0 \pm 3) \times 10^2$

All errors given in Table I are 1σ values and are those reported by SQUAD.[8] They should thus be considered minimum values associated with these experiments. Comparison of this work with prior literature data is possible at 25 and 50°C.[4,5] Within the errors quoted for the present results, agreement of the new technique with established methodology is judged to be quite satisfactory for the three Pr-digly stability constants. Such agreement serves as a general validation of the present experimental approach.

For the Pr-digly system, existing literature data are consistent with the van't Hoff relationship for all three complexes (i.e., $\ln K$ vs T^{-1} is linear). Reaction enthalpies and entropies can thus be calculated, and results of these computations for the three complexes over the range $t = 5-95^{\circ}\text{C}$ are presented in Table II.

Table II. Results of van't Hoff analyses of Pr-digly experimental data over the range $t = 5-95^{\circ}\text{C}$.

Complex (PrL ₁)	$-\Delta H_{101}$ (kJ/mol)	ΔS_{101} (J/mol-K)
i - 1	1.7 ± 0.3	97 ± 1
i - 2	3.5 ± 0.4	63 ± 1
i - 3	4.6 ± 0.5	33 ± 2

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