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# CHEMICAL SPECIATION OF Am, Cm AND Eu WITH EDTA AT HIGH IONIC STRENGTH

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## INTRODUCTION

The high level radioactive waste (HLW) stored in the DOE Hanford tanks are alkaline with high concentrations of $Na^+$ and reasonably high concentrations of organic chelators such as EDTA, HEDTA, Citric acid and NTA. For efficient, economical processing strategies of the HLW, thermodynamic data of Am, Cm and Eu with EDTA at high ionic strength is necessary to evaluate the species present. In this work the complexation of Am, Cm and Eu with EDTA at 5.0 M $NaClO_4$ and a pcH of 3.60 was studied over the temperature range of 0 to 60$^o$C. The stability constants of the complex formed have been evaluated and the thermodynamic parameters calculated. Time-resolved laser fluorescence spectroscopy studies of the Eu (III)-EDTA system at 5.0 M $NaClO_4$ have also been done.

## EXPERIMENTAL

The disodium salt of ethylendiaminetetraacetic acid (Fisher, ACS Certified) and sodium perchlorate (Aldrich ACS Certified) were used as received. Di(2-ethylhexyl)phosphoric acid, HDEHP (minimum 95% di-ester, Sigma Aldrich) was dissolved in heptane (Fisher, ACS) and diluted solutions of $5x10^{-4}$ or $2x10^{-4}$ M concentrations were used as extractants.

$^{241}$Am, $^{244}$Cm and $^{152,154}$Eu (from Oak Ridge National Laboratory) were used. The $NaClO_4$ solution prepared was 5.0 M and the pcH adjusted to 3.6 $\pm$ 0.02. The organic phase was pre-equilibrated with $NaClO_4$ solution. The aqueous phase (EDTA between

0.25 to $5.0 \times 10^{-5}$ M in 5.0 M $NaClO_4$ at pcH 3.60) containing one of the radioactive tracers was mixed with the same volume of the pre-equilibrated HDEHP/heptane solution at temperatures 0, 25, 35, 45 and 60 $\pm$ 0.1$^{o}$C. Afterwards, the solutions were centrifuged and 1.0 mL aliquots from the organic and aqueous phases withdrawn for radioassay. The equilibrium pH was measured and the pH meter reading (pHr) were converted to the hydrogen ion concentration at 5.0 M $NaClO_4$ ionic strength.

From the distribution ratio, $D = [M^{3+}]_{(o)}/[M^{3+}]_{(a)}$, at varying EDTA concentrations, the stability constant ($\beta_{101}$) of the complex formed was calculated using the equation:

$$/D_0/D-1 = \beta_{101}[L]/$$

where $D_0$ is the distribution ratio of metal ions in the absence of EDTA.

The thermodynamic parameters, $\Delta G$, $\Delta H$ and $\Delta S$ have been evaluated using temperature dependence of the log $\beta_{101}$ values.

The fluorescence spectroscopic measurements were done in 5.0 M $NaClO_4$ at varying Eu(III) and EDTA concentrations and also at varying pcH values between 3.6 to 9.0. The $^7F_0$ – $^5D_0$ excitation spectra of the Eu solutions were measured using an instrumental set up described in detail[1,2]. The excitation spectra were recorded by scanning the tunable dye laser stepwise at regular wavenumber intervals through the absorption band (577.7 – 580.7 nm) while monitoring the emission of $^7F_0$ – $^5D_0$ at 616 nm. Luminescence decay curves were acquired by averaging 1000 laser pulses with a digital oscilloscope while excitating at the peak of the $^7F_0$ – $^5D_0$ transition and monitoring the luminescence intensity at 616 nm.

## RESULTS AND DISCUSSION

Solvent extraction

From plots of 1/D vs $[EDTA]_{total}$ (Figure 1), straight lines were obtained for all the three metals at all the temperatures. This suggests that under the experimental conditions, the Am, Cm and Eu cations with EDTA formed the 1:1 complex. The stability constant ($\beta_{101}$) of the complexes are given in Table 1. These values are smaller than those reported at ionic strengths $\leq$ 1.0 M [3,4]. The stability constants increased with increasing temperature. The thermodynamic parameters, $\Delta H$ (19.7 kJ mol$^{-1}$) and $\Delta S$ (366 J mol$^{-1}$ K$^{-1}$) for the formation of Am complex are positive, indicating that the reaction is stabilized by the entropy change.

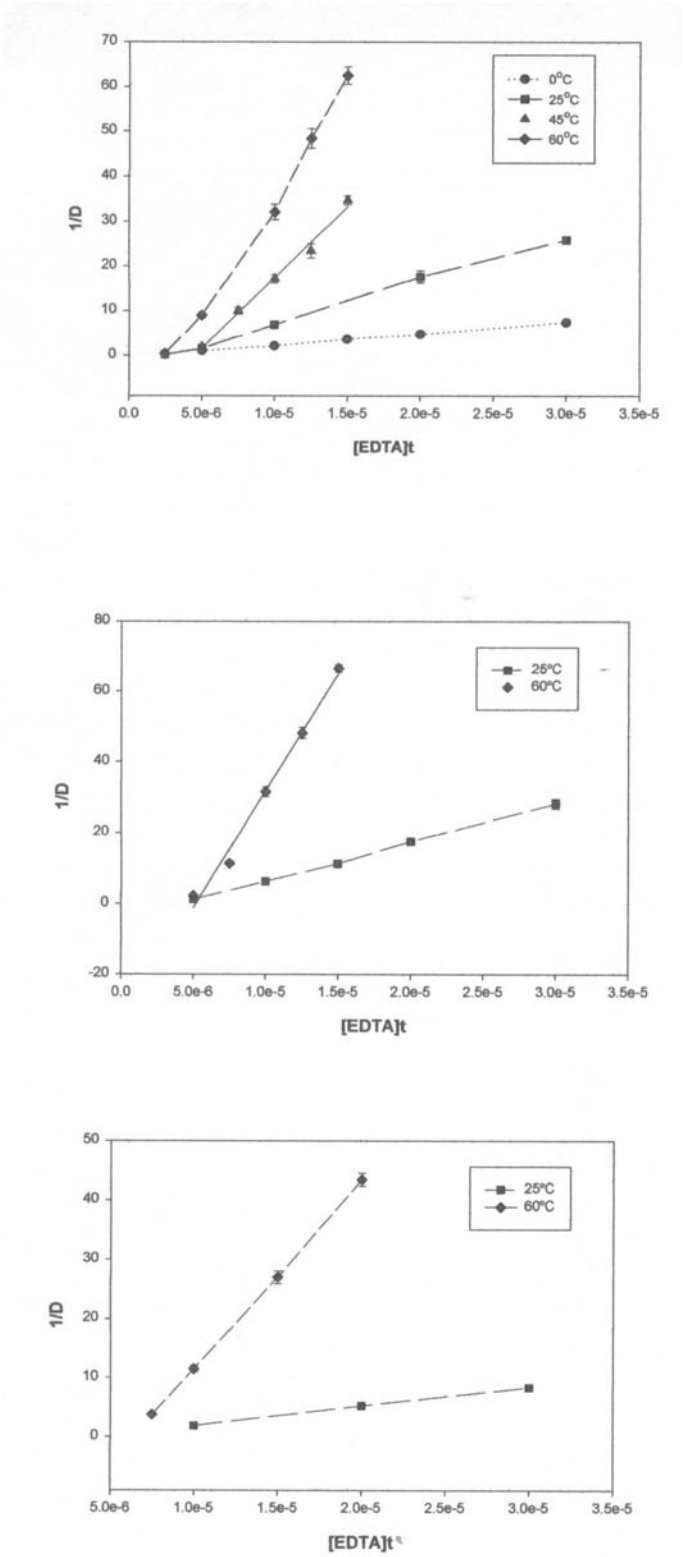


**Figure 1.** Plot of 1/D vs [EDTA]t at various temperatures for $Am^{3+}$, $Cm^{3+}$ and $Eu^{3+}$ at I = 5.0 M $NaClO_4$.

**Table 1.** Stability constant values of Am, Cm and Eu-EDTA complex at 5.0M $NaClO_4$ and varying temperature.

| Temperature ($^oC$) | log $\beta_{101}$, $M^{3+}$ Am | Cm | Eu |
|---|---|---|---|
| 0 | 15.45 ± 0.03 | - | - |
| 25 | 15.74 ± 0.03 | 15.88 ± 0.02 | 15.58 ± 0.02 |
| 45 | 15.88 ± 0.06 | - | - |
| 60 | 16.18 ± 0.06 | 16.43 ± 0.03 | 16.35 ± 0.02 |

Time-resolved laser fluorescence spectroscopy

The time-resolved laser fluorescence spectroscopy and lifetime measurements have established the formation of $EuEDTA(H_2O)_3^-$ between pcH 3.6 to 7.0 and $Eu(OH)(EDTA)(H_2O)_2^{2-}$ at pcH 9.0 in 5.0 M $NaClO_4$. These data in conjunction with further data to be generated on the thermodynamics and TRLFS studies of citrate and EDTA+citrate systems will be useful in the predictive modeling of the phase partitioning during tank processing.

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