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ARTICLE TYPE

## Spectrophotometric study of Am(III) complexation with nitrate in aqueous solutions at elevated temperatures

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The complexation of americium(III) with nitrate was studied at temperatures from 10 to 85 °C in 1 M HNO<sub>3</sub>/HClO<sub>4</sub> by spectrophotometry. The 1:1 complex species, AmNO<sub>3</sub><sup>2+</sup>, was identified and the stability constants were calculated from the absorption spectra collected by titrations at several temperatures. Specific ion interaction theory (SIT) was used for ionic strength corrections to obtain the stability constants of AmNO<sub>3</sub><sup>2+</sup> at infinite dilution and variable temperatures. The absorption spectra of Am(III) in diluted HClO<sub>4</sub> were also reviewed, and the molar absorptivity of Am(III) at around 503 nm and 813 nm were re-calibrated by titrations with standardized DTPA solutions to determine the concentration of Am(III).

### Introduction

In the last decade, even though there has been a short pause after the Fukushima accident, the development of nuclear energy is proceeding at a rapid rate resulting from its role as a major energy source that does not contribute to greenhouse gas emissions.<sup>1</sup> However, the problems of safely handling and disposing the spent nuclear fuel and the ultimate disposition of high level nuclear waste still remains, causing public concern in some countries about the desirability of nuclear energy. To minimize radioactive waste, to more effectively manage global nuclear resources, as well as to reduce the risk of nuclear weapon proliferation, the spent fuel might be reprocessed, the fissile materials U and Pu might be recovered for making new fuel, and the small amount of minor actinides, Am and Cm, might be separated for further treatment such as transmutation.

For transmutation, at first Am and Cm should be separated from each other after being separated as a group from other actinides and fission products, such as lanthanides, resulting from their different behavior in fast neutron reactors and accelerator driven systems for transmutation.<sup>2</sup> The separation of Am and Cm from each other has been a great challenge because of the nearly identical chemical properties of Am(III) and Cm(III) and the very unstable oxidation states of Am other than +3 in the presence of organic materials, such as organic resins, solvents, and ligands. To develop effective processes for the separation of Am and Cm, precise methods and techniques are needed to detect the subtle difference in solution chemistry between Am(III) and Cm(III), and to generate accurate thermodynamic data for models and simulation. Currently, thermodynamic data for Am(III) are scarce, and Cm(III), Nd(III) and Eu(III) are often used as surrogates for Am(III) when the separation of Am(III) from Cm(III) and Ln(III) is not the main objective.<sup>3-6</sup> In spent fuel reprocessing, Am(III), Cm(III) and some Ln(III) are

usually present in aqueous solutions containing nitric acid at elevated temperatures. In addition, concentrated nitrate is often used as the “background” electrolyte in complexation studies of actinides and lanthanides. Therefore, thermodynamic parameters of actinide complexes with nitrate are needed to calculate the stability constants and enthalpies of formation for actinide complexes with other ligands.

The structural and thermodynamic characterization of Nd(III), Eu(III), and Cm(III) complexes with several ligands in solution at different temperatures employing spectrophotometry have been conducted in the past several years.<sup>7-10</sup> This convenient method allows the simultaneous determination of stability constants and the enthalpy change for weak complexation by the van't Hoff method. Building on the experience in previous work, this study investigates the complexation of Am(III) with nitrate by spectrophotometry at temperatures from 10 to 85 °C in aqueous solutions of 1 M ionic strength. The purpose of this work is twofold. First, the stability constants of the 1:1 Am(III) complex with nitrate, AmNO<sub>3</sub><sup>2+</sup>, is determined at temperatures from 10 to 85 °C by spectrophotometry and the effect of temperature on the complexation is evaluated. Second, the UV-Vis absorption spectra of Am(III) in HClO<sub>4</sub>/HNO<sub>3</sub> are collected, then compared to spectra obtained in previous studies, and the molar absorptivity of Am(III) in the UV/Vis region is reviewed and standardized for future studies.

The Am(III) ion has two prominent bands in the visible region. One of these is at 503 nm and the other at 813 nm. Both bands are sensitive to the Am(III) coordination environment, being shifted or split due to the ligand complexation by the presence of ligands. However, even though spectrophotometry has proven to be useful for investigating the complexation of Am(III), the values of the molar absorptivity for the sharp band at 503 nm range from 350 to 430 cm<sup>-1</sup> M<sup>-1</sup> in previous studies as a result of limited instrumental resolution and the high activity of the two common

isotopes of Am used in previous investigations.<sup>11-18</sup>

## Experimental

### Chemicals and Sample Preparation

The americium used in this work is carrier-free <sup>243</sup>Am. The samples of Am(III) were prepared as follows. A 0.1 mL solution of 0.01 M HCl containing about 0.01-0.1 mg of Am(III) was dried in a small vial at about 150 °C on a hot plate and the residue was dissolved with 0.5 mL of 0.01 M HClO<sub>4</sub> in a fuming hood or in a glove-box. The drying and dissolving process was repeated twice to convert AmCl<sub>3</sub> to Am(ClO<sub>4</sub>)<sub>3</sub>. Then, the residue was dissolved with 1 mL of various acid solutions. For the spectrophotometric titrations, a set of six samples, each containing the same amount of Am(III), were prepared by dissolving the dried Am(ClO<sub>4</sub>)<sub>3</sub> residual into 1 mL of one of the six mixtures of 1M HClO<sub>4</sub> – 1M HNO<sub>3</sub> in which the volume fractions of 1M HNO<sub>3</sub> are 0, 0.200, 0.400, 0.600, 0.800, and 1.000, corresponding to the concentration of HNO<sub>3</sub> of 0, 0.200, 0.400, 0.600, 0.800, and 1.000 M.

For determining the concentration of Am(III) and the molar absorptivity in dilute HClO<sub>4</sub>, two Am(III) samples were prepared by dissolving the dried AmCl<sub>3</sub> into 0.001 M HClO<sub>4</sub> and titrated with a 0.001 M standard DTPA solution. The concentrations of Am(III) in the samples in HClO<sub>4</sub> solution were calculated with absorption spectrophotometry using the molar absorptivity of Am(III) in perchloric acid solutions ( $\epsilon = 423 \text{ cm}^{-1} \text{ M}^{-1}$  at 503.2 nm, see below).

### Absorption Spectra

The absorption spectra of Am(III) in acid solutions at different temperatures were collected on a Cary6000i spectrometer in the wavelength region between 350 to 900 nm (0.05 nm interval and 0.2 nm spectral band width (SBW)). Quartz cells of 10 mm path length were used. The temperature of the sample was controlled within  $\pm 0.2$  °C with a temperature controller. The stability constant of the Am(III)/nitrate complex (in molarity scale) was calculated by nonlinear least-squares regression using the Hyperquad program.<sup>19</sup>

## Results and discussion

### Re-calibration of the molar absorptivity of Am(III)

The 503 nm peak of Am(III) is quite narrow (FWHM = 5.25 nm). In previous studies, the molar absorptivity at 503 nm was reported from 350 to 430  $\text{cm}^{-1} \text{ M}^{-1}$ .<sup>11-18</sup> It was also found that this absorption band does not follow the Beer-Lambert law, which was ascribed to an instrumental effect: the spectrophotometer-selected SBW is too large for the narrow 503 nm peak.<sup>14</sup>

Figure 1 illustrates the effect of the selected SBW on the optical density of the 503 nm peak. The observed peak height increases as the SBW is decreased. However, when the SBW is set at less than 0.3 nm, there is no further increase in peak height at 503 nm. This shows that the normal SBW in most previous studies, corresponding to a dispersion of 1 nm or more, is insufficient to resolve the feature and therefore properly obtain the peak area. All further measurements in this work were conducted with a 0.2

nm SBW and 0.05 nm interval as the standard set-up.

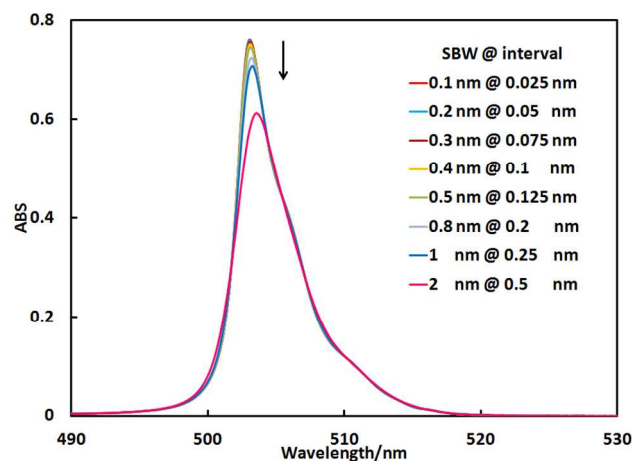


Figure 1 The effect of the spectral band width (SBW) on the absorption at 503 nm.

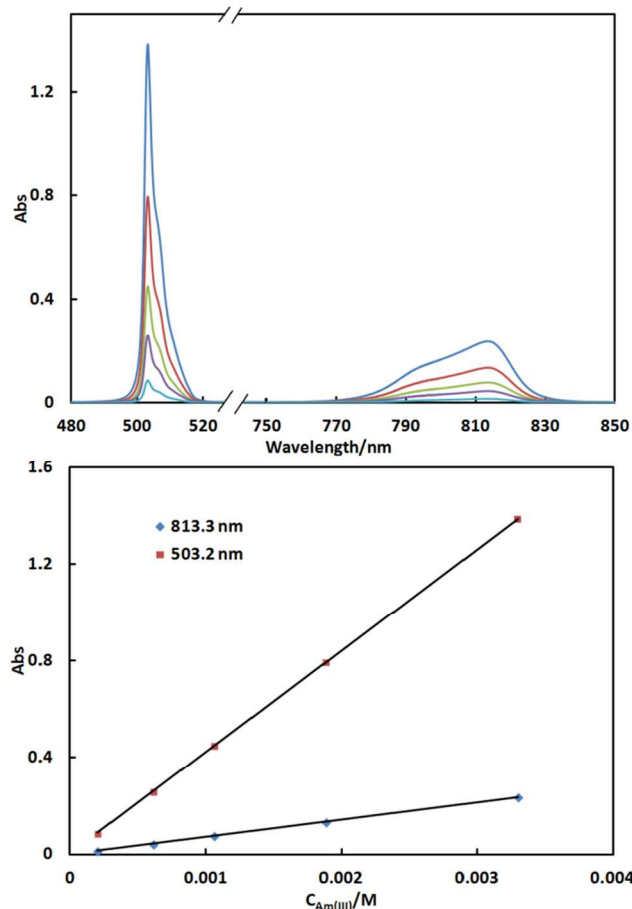


Figure 2 Absorption spectra of Am(III) at varying concentrations: 0.204, 0.608, 1.06, 1.88, 3.27 mM (Upper), and the plots of absorption at 503.2 and 813.3 nm against Am(III) concentration.

Utilizing a SBW of 0.2 nm and small interval step of 0.05 nm, the optical properties of the two prominent bands of Am(III) were re-investigated. A relatively concentrated Am(III) stock solution in 1 mM HClO<sub>4</sub> was prepared. The absorption spectra from several dilutions of this stock solution were measured in the 503 nm and 813 nm peak regions. The results are plotted in Figure 2, and the

excellent linearity of the plots of absorption against concentration indicate that the Beer-Lambert law is obeyed for both the sharp 503 nm and the broad 813 nm features.

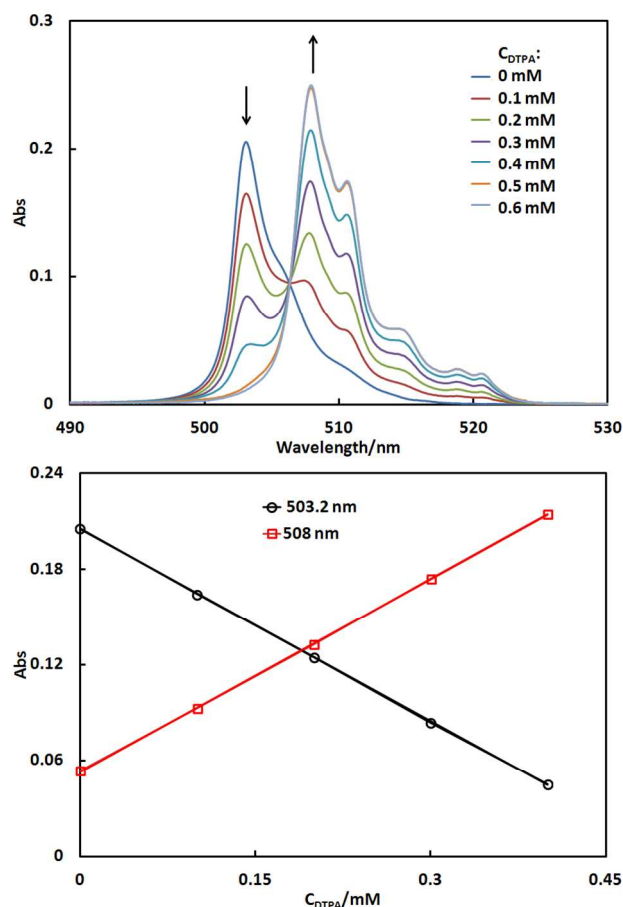


Figure 3 Representative spectra of Am(III) titrated with standardized DTPA solutions (Upper), and the plot of absorption against DTPA concentration (Lower).

To further verify the molar absorptivity of Am(III) in the UV-Vis region, titrations of Am(III) with a standardized DTPA solution were conducted by monitoring the variation of absorption band of Am(III) at about 503 nm. As shown in Figure 3, as DTPA concentration increased, the 503 nm peak for free Am(III) decreased and a new peak at 508 nm is evident, and an isobestic point was obtained at 506.3 nm. The absorptions at 503.2 nm and 508 nm are plotted against DTPA concentration. The excellent linearity of the plots suggests that DTPA quantitatively forms a complex with Am(III) until all the Am(III) ions are completely consumed. The concentration of Am(III) is calculated using equation (1):

$$C_{\text{Am}} = C_{\text{DTPA}} \times (A_0 - A_{\infty}) / B_{503\text{nm}} \quad (1)$$

where  $A_0$  and  $A_{\infty}$  is the absorption at 503.2 nm, respectively for the solution at the beginning and the end of the titration.  $B_{503\text{nm}}$  is the slope determined from the linear fit of the plot. The molar absorptivity at 503.2 nm is calculated to be  $423 \pm 4 \text{ cm}^{-1} \text{ M}^{-1}$ . Combined with the information from Figure 1, the molar absorptivity at 813.3 nm is calculated to be  $71.3 \pm 1 \text{ cm}^{-1} \text{ M}^{-1}$ . The determined molar absorptivity value of  $423 \pm 4 \text{ cm}^{-1} \text{ M}^{-1}$  at

503.2 nm is in good agreement with the value of  $426 \pm 4 \text{ cm}^{-1} \text{ M}^{-1}$  obtained from coulometric titration and EDTA complexometric titration, while the value of  $71.3 \pm 1 \text{ cm}^{-1} \text{ M}^{-1}$  for the band at 813 nm is much higher the value of  $60 \text{ cm}^{-1} \text{ M}^{-1}$  reported in the literature.

### Stability Constants of $\text{AmNO}_3^{2+}$ at Variable Temperatures

Figure 4 shows the absorption spectra of two representative titrations of Am(III) with nitrate at 10 and 85 °C. Only the sharp absorption band around 503 nm corresponding to the  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  transition of Am(III) is monitored in the titrations with nitrate because it is more sensitive to the coordination environment. At each temperature, the  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  transition was slightly red-shifted as the concentration of nitrate was increased, while the integrated area of the band was almost the same. Factor analysis by the Hyperquad program indicated that there are two absorbing species of Am(III), and the spectra were best-fit with the formation of  $\text{AmNO}_3^{2+}$  as described by equation (2).



Deconvoluted spectra of  $\text{Am}^{3+}$  and  $\text{AmNO}_3^{2+}$  at 10 and 85 °C are shown in the lower part of Figure 4. The spectra at intermediate temperatures are not shown, but the trends in the spectral features are similar at each temperature except for the integrated areas of the band that slightly decrease with elevated temperatures.

The formation constants of  $\text{AmNO}_3^{2+}$  at 10, 25, 40, 55, 70 and 85 °C are calculated and listed in Table 1. Literature values at different ionic strengths at around 25 °C are also included for comparison. The variation of the spectra in Figure 4 and the calculated stability constants in Table 1 indicate that the complexation of Am(III) with nitrate is quite weak, and it is minimally affected by temperature from 10 to 85 °C. The literature values measured by ion exchange method or distribution method at 22-30 °C are slightly higher than the value in this work at 25 °C. The difference might be ascribed to the factor that only the inner-sphere complex is counted by spectrophotometric method while both out-sphere and inner-sphere complexes are taken account by ion exchange method or distribution method.

To convert the stability constants measured at 1 M ionic strength to the values at the standard state preferred by common compilations of thermodynamic data, the specific ion interaction (SIT) approach has been used to calculate the formation constants at zero ionic strength. The detailed approaches and procedures are described elsewhere and the formation constants in molarity ( $\log K$ ) are adopted in molality ( $\log K_m$ ) without further correction.<sup>6,10</sup>

To quantitatively evaluate the effect of temperature on the complexation of Am(III) with nitrate, the  $\log K$  vs.  $1/T$  are plotted in Figure 5 (van't Hoff plot). The excellent linearity of the van't Hoff plot indicates the enthalpy of the complexation is nearly constant in the temperature range (10-85 °C). From the linear fit of the plot, the enthalpy for the reaction described in equation (2) at standard state was calculated to be  $2.0 \pm 0.5 \text{ kJ/mol}$ . The temperature effect and the enthalpy for complexation with nitrate for Am(III) much more closely resemble those for Nd(III) than for Cm(III).<sup>8,10</sup>

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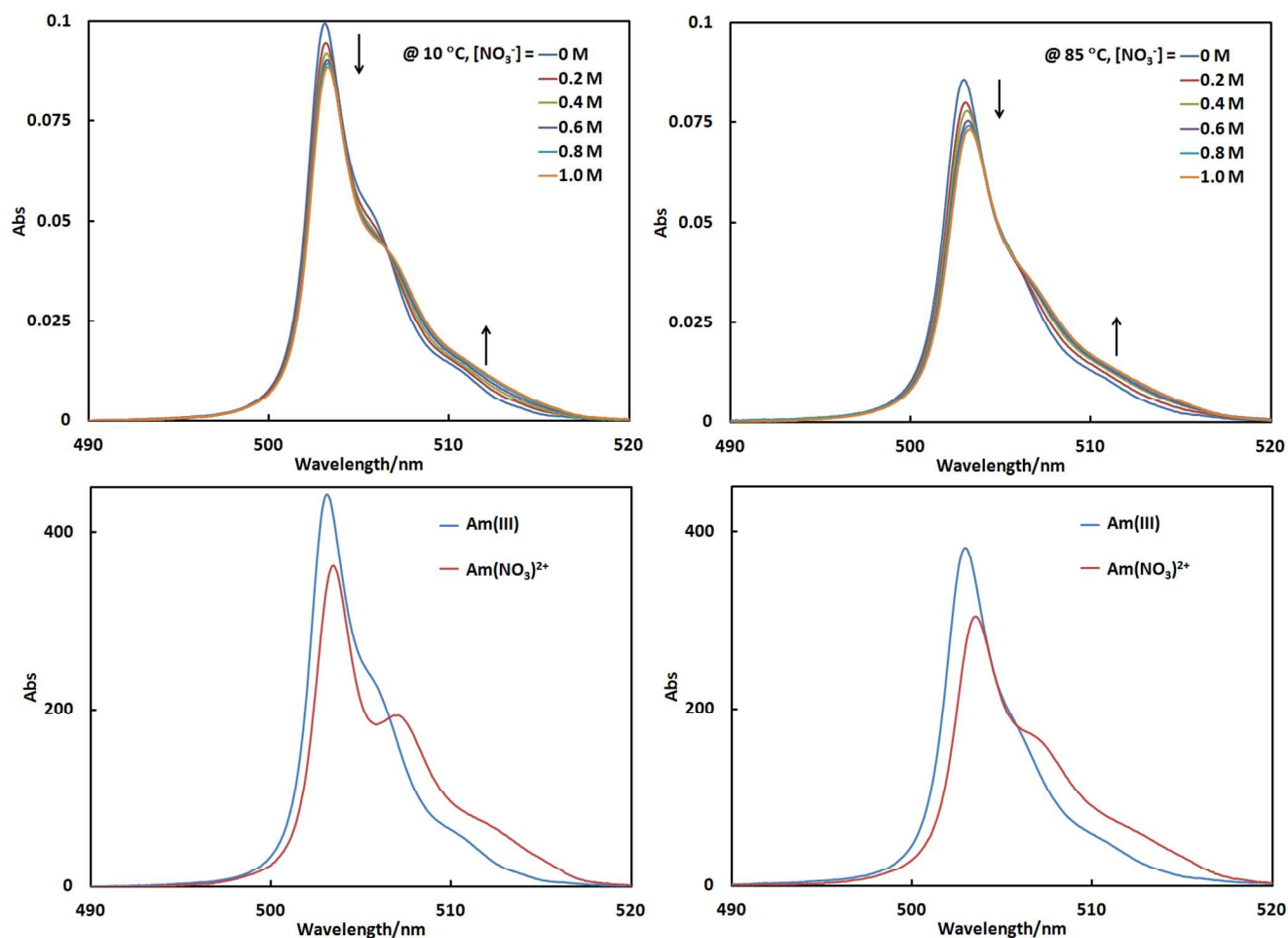
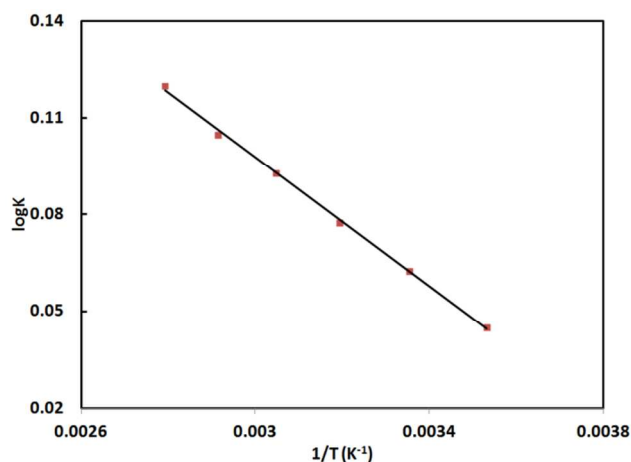


Figure 4. Representative spectra of Am(III) titrated with nitrate.  $V^0 = 1.0$  mL, 0.224 mM Am(III) in 1 M  $\text{HClO}_4/\text{HNO}_3$ . Upper: Spectra collected during titrations; Lower: Molar absorptivities obtained from spectra deconvolution (left: at 10 °C, right: at 85 °C).



5 Figure 5.  $\log K$  vs  $1/T$  for Am(III)/nitrate complexation.  $I = 1.0$  M  $\text{H}(\text{ClO}_4/\text{NO}_3)$ .

### Summary

The UV/Vis absorption of Am(III) was re-visited. The molar absorptivity of Am(III) in diluted  $\text{HClO}_4$  was determined to be  $423 \pm 4 \text{ cm}^{-1} \text{ M}^{-1}$  at 503 nm and  $71.3 \pm 1 \text{ cm}^{-1} \text{ M}^{-1}$  at 813 nm by complexometric titration with DTPA. To obtain proper optical absorption for the sharp peak of Am(III) at 503 nm, a SBW less than 0.3 nm should be utilized for the collection of spectra. Spectroscopic and thermodynamic data indicate nitrate forms an inner-sphere Am(III) complex which is slightly enhanced with increasing temperature from 10 to 85 °C. The information and data from this investigation will help develop reliable methods for studying the complexation of Am(III) with other ligands in nitrate solutions at variable temperatures.

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**Table 1** Thermodynamic data of Am(III) complexation with nitrate at different temperatures ( $\text{Am}^{3+} + \text{NO}_3^- = \text{AmNO}_3^{2+}$ ), t.w. – this work.

T/C	Ionic medium	log K	Method*	log $K_m^0$	$\Delta H$ kJ·mol <sup>-1</sup>	$\Delta S$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	Ref.
10	1 M HClO <sub>4</sub> /HNO <sub>3</sub>	0.045 ± 0.05	Spec.	1.09 ± 0.06			t.w.
25	1 M HClO <sub>4</sub> /HNO <sub>3</sub>	0.063 ± 0.05	Spec.	1.13 ± 0.06	2.0 ± 1	9.5 ± 3	t.w.
40	1 M HClO <sub>4</sub> /HNO <sub>3</sub>	0.078 ± 0.05	Spec.	1.19 ± 0.06			t.w.
55	1 M HClO <sub>4</sub> /HNO <sub>3</sub>	0.093 ± 0.05	Spec.	1.24 ± 0.06			t.w.
70	1 M HClO <sub>4</sub> /HNO <sub>3</sub>	0.105 ± 0.05	Spec.	1.30 ± 0.06			t.w.
85	1 M HClO <sub>4</sub> /HNO <sub>3</sub>	0.125 ± 0.05	Spec.	1.36 ± 0.06			t.w.
22	1 M HClO <sub>4</sub> /HNO <sub>3</sub>	0.25 ± 0.06	Dist.				[5]
26	1 M HClO <sub>4</sub> /HNO <sub>3</sub>	0.15 ± 0.06	Ion Exch.				[20]
26	1 M NaClO <sub>4</sub> /NaNO <sub>3</sub>	0.20 ± 0.06	Ion Exch.				[20]
30	1 M LiClO <sub>4</sub> /LiNO <sub>3</sub>	0.30 ± 0.04	Dist.				[3]
30	1 M HClO <sub>4</sub> /HNO <sub>3</sub>	0.29 ± 0.04	Dist.				[3]
30	1 M NaClO <sub>4</sub> /NaNO <sub>3</sub>	0.26 ± 0.04	Dist.				[3]
30	1 M NH <sub>4</sub> ClO <sub>4</sub> /NH <sub>4</sub> NO <sub>3</sub>	0.23 ± 0.04	Dist.				[3]

\*Spec. – spectrophotometry; Ion Exch. – ion exchange; Dist. – solvent-solvent extraction distribution.

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