Determine rate of reaction of hydroxyl radical with carboxylic acids and polyaminocarboxylates

Fuel Cycle Technology

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SUMMARY

In the Advanced TALSPEAK process, the bis(2-ethylhexyl)phosphoric acid (HDEHP) extractant used in the traditional TALSPEAK process is replaced by the extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]). In addition, the aqueous phase complexant and buffer used in traditional TALSPEAK is replaced with the combination of N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA) and citric acid. In order to evaluate the possible impacts of gamma radiolysis upon the efficacy of the Advanced TALSPEAK flowsheet, aqueous and organic phases corresponding to the extraction section of the proposed flowsheet were irradiated in the INL test loop under an ambient atmosphere.

The results of these studies conducted at INL, led INL researchers to conclude that the scarcity of values of rate constants for the reaction of hydroxyl radical with the components of the Advanced TALSPEAK process chemistry was severely limiting the interpretation of the results of radiolysis studies performed at the INL. In this work, the rate of reaction of hydroxyl radical with citric acid at several pH and HEDTA at several pH values was measured using a competitive pulse radiolysis technique. The results reported here demonstrate the importance of obtaining hydroxyl radical reaction rate data for the conditions that closely resemble actual solution conditions expected to be used in an actual solvent extraction process. This report describes those results and is written in completion of milestone M3FT-17IN030102014.

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ACRONYMS

CA   Citric acid

DTPA   Diethylenetriaminepentaacetic acid

FCR&D   Fuel Cycle Research and Development program

HDEHP   Bis(2-ethylhexyl)phosphoric acid

HEDTA   N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid

HEH[EHP]   2-ethyl(hexyl)phosphonic acid mono-2-ethylhexyl ester

INL   Idaho National Laboratory

LA   Lactic Acid

SCN^- Thiocyanate anion

TALSPEAK   Trivalent Actinide Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes

TRUEX   TRansUranic EXtraction process

EVALUATE THE ROLE OF ORGANIC ACIDS IN THE PROTECTION OF LIGANDS FROM RADIOLYTIC DEGRADATION

1. INTRODUCTION

Separating the minor actinide elements (americium and curium) from the fission product lanthanides is an important step in closing the nuclear fuel cycle. Isolating the minor actinides will allow transmuting them to short lived or stable isotopes in fast reactors, thereby reducing the long-term hazard associated with these elements.[1-2] A two-step method is being considered by the Fuel Cycle Research and Development (FCR&D) program to separate the minor actinides from acidic high-level waste. The first step involves co-extracting the lanthanides and minor actinides using the transuranic extraction (TRUEX) process.[3] The second step uses the Trivalent Actinide-Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Complexes (TALSPEAK) process to separate the minor actinides from the lanthanides.[4-5] The tandem TRUEX–TALSPEAK approach has been demonstrated on irradiated fuel at a laboratory scale.[6] However, the TALSPEAK process suffers the disadvantage of slow extraction and stripping kinetics and high sensitivity to the aqueous phase pH. To overcome these disadvantages, a variation of the TALSPEAK process has been proposed which replaces the traditionally used bis(2-ethylhexyl)phosphoric acid (HDEHP) extractant with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]).[7] In addition, the aqueous phase complexant and buffer used in traditional TALSPEAK are replaced with the combination of N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA) and citric acid. This is referred to as the Advanced TALSPEAK process. The key advantages of Advanced TALSPEAK process are reported to be less dependence of the process performance on the aqueous solution pH, more predictable extraction behavior, and more rapid extraction kinetics. The structures of the compounds utilized in this process are shown in Figure 1.

N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid
(HEDTA)

Citric acid
(CA)

2-ethyl(hexyl)phosphonic acid mono-2-ethylhexyl ester
(HEH[EHP])
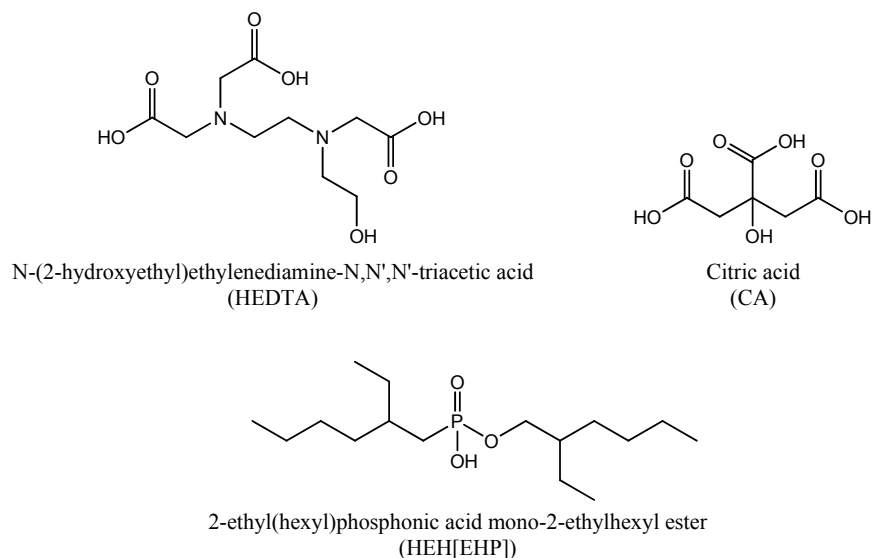
Figure 1. Structures of compounds used in the Advanced TALSPEAK process.

In order to evaluate the possible impacts of radiation damage upon the efficacy of the Advanced TALSPEAK flowsheet, aqueous and organic phases corresponding to the extraction section of the proposed flowsheet were irradiated in the INL test loop under an ambient atmosphere and by air-sparged static irradiations. A suite of analytical techniques were employed to determine the variation in composition as a function of absorbed γ-dose and in some cases identify the radiolytically produced species. Samples of the

irradiated aqueous and organic phases were spiked with americium and europium radiotracers and distribution ratios (D_{Am} and $D_{Eu)}$ were determined as a function of absorbed dose.[8]

Results from this earlier study performed at the INL[9] suggested that different carboxylic acid buffers employed in the TALSPEAK and Advanced TALSPEAK process chemistries (citric acid versus lactic acid) lead to differing extents of radiolytic degradation of the aminopolycarboxylate (HEDTA) aqueous soluble complexant. Based upon those observations, the rate of reaction of hydroxyl radical with citric acid was measured. This report describes those results and is written in completion of milestone M3FT-17IN030102014, the goal of which was to evaluate the role of organic acids in the protection of ligands from radiolytic degradation.

2.   EXPERIMENTAL

All chemicals (Aldrich) used in the study were reagent grade or higher and used as received without further purification. Solutions were made with ultrapure deionized water ($\geq$ 18 MΩ) obtained from a Millipore Milli-Q system.

The measurements of hydroxyl radical reaction rate constants were performed using the linear accelerator (LINAC) electron pulse radiolysis system at the Radiation Laboratory, University of Notre Dame. The irradiation and transient absorption detection system has been described elsewhere.[10] Dosimetry[11] was performed on N_2O saturated solutions of KSCN (1.00 x 10^{-2} M) at λ = 475 nm ($G\varepsilon$ = 5.2 x 10^{-4} m^{2}J^{-1}), with an average dose of 3 – 5 Gy per 2 – 3 ns pulse.

Temperature control of the solutions was achieved by flowing the ambient temperature solutions through a short temperature controlled condenser prior to irradiation. The solution temperature was measured immediately post irradiation using a thermocouple placed directly in the flow.[12] Temperature stability of this system was $\pm$ 0.1 °C.

3.   RESULTS AND DISCUSSION

For the γ-radiolysis of acidic (nitric acid) aqueous and organic (paraffinic) mixtures, the hydroxyl radical is the predominate radical species present in solution.[13] The primary mode of interaction between hydroxyl radical and aminopolycarboxylic and carboxylic acids is H-atom abstraction from the ligand. The rate constants for H-atom abstraction, k, by hydroxyl radical[14] for compounds relevant to the TALSPEAK and Advanced TALSPEAK, ALSEP processes are listed in Table 1. The majority of these rate constants listed in Table 1 were not obtained under process relevant conditions.

Table 1. Rate constants for the H-atom abstraction by hydroxyl radical for several aminopolycarboxylic and carboxyl acids.

Species	k, L·mol^{-1}·s^{-1}
EDTA^{2-}, pH = 4	4.0 x 10^8
EDTA^{3-}, pH = 9	2.0 x 10^9
DTPA, pH ~ 7	2.3 x 10^9
HEDTA, pH ~ 0	1.1 x 10^{10}
Citric acid, pH ~ 1	5.0 x 10^7
Lactic acid, pH ~ 1	4.3 x 10^8

From the values listed in Table 1, it is clear that aminopolycarboxylic acids react rapidly with hydroxyl radical. In the case of HEDTA, the rate of reaction with hydroxyl radical is essentially diffusion controlled.

Carboxylic acids react more slowly with hydroxyl radical in solution. A relative rate analysis for the TALSPEAK and Advanced TALSPEAK systems shows the rate of reaction of lactic acid (LA) with hydroxyl radical is approximately 65 times faster than the rate of reaction of citric acid (CA) with hydroxyl radical (1.5 M LA x k_{LA} versus 0.2 M CA x k_{CA}). The higher relative rate calculated for the TALSPEAK system indicates the high concentration of LA may serve to protect the TALSPEAK solvent from radiolytic degradation by acting as a hydroxyl radical scavenger. The slower rate of reaction for citric acid with the hydroxyl radical and the lower concentration of the carboxylic acid buffer used in the Advanced TALSPEAK process likely accounts for the observed significant increase in D_{Am} versus absorbed dose.[9] This can be attributed to a decrease in HEDTA concentration caused by its reaction with hydroxyl radical; since HEDTA functions as an actinide "holdback" reagent, the consumption of HEDTA by H-atom abstraction by the hydroxyl radical results in higher D_{Am} and lower $^{Eu}S_{Am}$ values.

In order to gain a more detailed understanding the rates of reactions important to the Advanced TALSPEAK process, the rate of reaction of hydroxyl radical with citric acid was measured under process relevant conditions. The kinetics of this reaction were explored by competitive methods using KSCN as a standard; whose rate constant[14] has been well-established as a function of temperature. At 25°C this reaction is:

$$\cdot OH + SCN^- (+ SCN^-) \rightarrow (SCN)_2^{-\cdot} + OH^- \qquad k_1 = 1.15 \times 10^{10} \ M^{-1} \ s^{-1} \qquad (1)$$

Typical kinetic data are shown in Figure 1. It is seen that with the addition of citric acid, the $(SCN)_2^{-\cdot}$ absorbance intensity at 475 nm decreases (Figure 1 top). By analyzing the reaction

$$\cdot OH + citric\ acid \rightarrow products \qquad k_2 = ? \qquad (2)$$

in competition with the hydroxyl radical reaction with thiocyanate we obtain the expression:

$$\frac{Abs^o}{Abs} = 1 + \frac{k_2[CA]}{k_1[SCN^-]} \qquad (3)$$

where Abs^o is the transient absorbance in the absence of any added citric acid, and Abs is the reduced absorbance in its presence. The transformed linear plot of Abs^o/Abs vs. $[CA]/[SCN^-]$ is seen in Figure 1 (bottom). From the linear fit to these data, we obtain an overall rate constant of $k_2 = (1.14 \pm 0.02) \times 10^8$ $M^{-1} \ s^{-1}$.
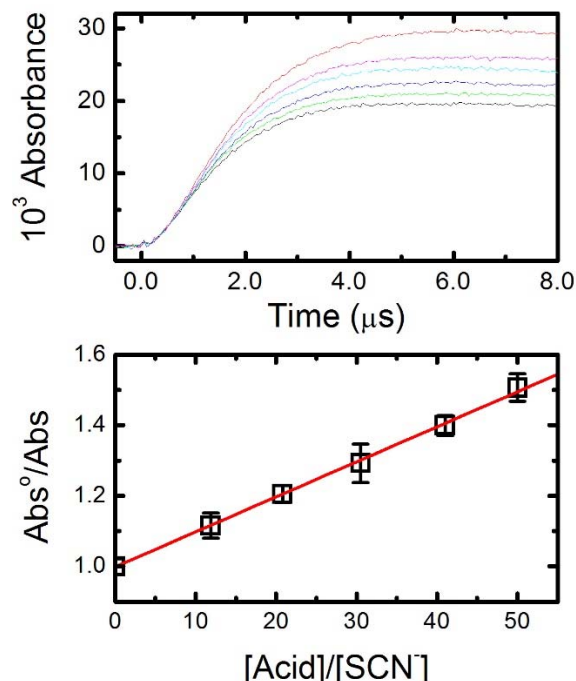
Figure 1. Top: Transient kinetic data for $(SCN)_2^{-\bullet}$ transient absorbance measured at 475 nm at 22.4°C and pH 4.657. From top to bottom curves depict individual profiles for zero, 1.19 mM, 2.08 mM, 3.05 mM, 4.10 mM and 5.00 mM added citric acid. Bottom: transformed competition kinetics data from peak intensities of individual curves shown in top plot. Solid line is weighted linear fit, with slope of (1.00 ± 0.02) x 10^{-2}, $R^2 = 1.00$. This slope corresponds to an overall rate constant of $k_2 = (1.14 \pm 0.02)$ x 10^8 M^{-1} s^{-1} under these conditions.

During FY-2016, the reaction rate of the OH• radical with citric acid was measured at several pH values and these data were used to calculate the individual k' rate constants for the reaction of OH• with the different citric species present in solution as pH varies.[15] The individual rate constants determined in that work are listed in Table 2.

Table 2. Values of the individual k' rate constants for the reaction of hydroxyl radical with citric acid.

Species	Rate constant	Calculated value M^{-1} s^{-1}
H_3A	k'_4	7.65 x 10^7
H_2A^-	k'_3	7.61 x 10^7
HA_2^-	k'_2	1.62 x 10^8
A_3^-	k'_1	2.80 x 10^8

The value of $k'_1 = 7.65$ x ^{1} (determined at pH = 3.33) agrees fairly well with the rate constant reported (5.0 x 10^7 M^{-1} s^{-1}) by Buxton et al. (determined at pH ~ 1),[14] however, it is approximately a factor of two higher than the value reported by Anbar and Neta[16] of 3.0 x 10^7 $M^{-1}s^{-1}$. Interesting, the reaction rate determined for citric using a solution pH relevant to actual process conditions, is approximately an order of magnitude slower than the hydroxyl radical reaction rate determined by Martin et al. for lactic acid using TALSPEAK process conditions (7.77 x 10^8 $M^{-1}s^{-1}$). Since the TALSPEAK, Advanced TALSPEAK, and ALSEP stripping sections are operated at a pH in the range of 3 – 4, these recent rate constant determinations demonstrate the importance of measuring these reaction rates under process relevant conditions.

Current efforts have focused upon the determination of the reaction rates of OH• with citric acid as a function of temperature and the determination of the reaction rates of OH• with HEDTA at several pH values. The rate coefficients for the reaction of citric acid with OH• as a function of pH and temperature

are shown in Table 3. The individual k' rate constants for the reaction of hydroxyl radical with citric acid at different temperatures are shown in Table 4. The rate coefficients for the reaction of HEDTA with OH• as a function of pH are shown in Table 5. The individual k' rate constants for the reaction of hydroxyl radical with the different HEDTA species present in solution as the pH is varied are shown in Table 6.

Table 3. Rate coefficients for the reaction of citric acid with OH• as a function of solution pH and temperature.

Temperature ($°C \pm 0.1 °C$)	pH	Rate coefficient $M^{-1}s^{-1}$	Error $\pm M^{-1}s^{-1}$
8.8	3.33	6.06×10^7	5.56×10^6
8.8	3.82	1.04×10^8	1.19×10^6
8.8	4.40	9.72×10^7	2.40×10^6
8.8	6.41	1.60×10^8	1.06×10^6
20.0	3.33	7.81×10^7	4.11×10^6
20.0	3.82	8.36×10^7	4.41×10^6
20.0	4.66	1.14×10^8	2.11×10^6
20.0	6.39	2.19×10^8	6.34×10^6
30.0	3.33	8.34×10^7	3.93×10^6
30.0	3.82	9.32×10^7	7.63×10^6
30.0	4.65	1.45×10^8	4.38×10^6
30.0	6.36	2.42×10^8	1.34×10^7
40.0	3.33	9.16×10^7	1.48×10^6
40.0	3.83	1.13×10^8	2.00×10^6
40.0	4.66	1.45×10^8	3.23×10^6
40.0	6.39	2.58×10^8	2.05×10^6

Table 4. Values of the individual k' rate constants for the reaction of hydroxyl radical with different citric acid species as a function of temperature.

Species	Temperature (°C ± 0.1 °C)	Rate Constant	Calculated value $M^{-1}s^{-1}$
H_3A	20.0	k'_4	7.65×10^7
H_2A^-		k'_3	7.61×10^7
HA_2^-		k'_2	1.62×10^8
A_3^-		k'_1	2.80×10^8
H_3A	30.0	k'_4	7.94×10^7
H_2A^-		k'_3	8.06×10^7
HA_2^-		k'_2	2.30×10^8
A_3^-		k'_1	2.59×10^8
H_3A	40.0	k'_4	4.23×10^7
H_2A^-		k'_3	1.20×10^8
HA_2^-		k'_2	1.78×10^8
A_3^-		k'_1	3.41×10^8

Table 5. Rate coefficients for the reaction of HEDTA with OH• as a function of solution pH determined at 20.0 ± 0.1 °C.

pH	Rate coefficient $M^{-1}s^{-1}$	Error $\pm M^{-1}s^{-1}$
3.00	1.86×10^8	8.08×10^6
5.40	1.94×10^9	5.23×10^7
7.79	3.64×10^9	2.74×10^7
9.79	3.93×10^9	8.92×10^7

Table 6. Values of the individual k' rate constants for the reaction of hydroxyl radical with different HEDTA species present in solution as pH varies, determined at 20.0 ± 0.1 °C.

Species	Rate Constant	Calculated Value $\pm M^{-1}s^{-1}$
H_3A	k'_4	1.03×10^8
H_2A^-	k'_3	1.99×10^8
HA_2^-	k'_2	3.64×10^9
A_3^-	k'_1	3.99×10^9

The rate constant for the H-atom abstraction by hydroxyl radical for HEDTA (see Table 1) is 1.1×1^{-10} $L \cdot mol^{-1} \cdot s^{-1}$ at pH ~ 0. At pH = 3, the measured rate constant for the reaction of OH• with HEDTA has decreased by two orders of magnitude (see Table 5). This observation points out the importance of measuring reaction rate constants for the reactions of carboxylic acids and aminopolycarboxylates at pH values relevant to actual conditions that would be encountered in actual process conditions.

4.   CONCLUSIONS AND CONTINUING WORK

In the Advanced TALSPEAK process, the bis(2-ethylhexyl)phosphoric acid (HDEHP) extractant used in the traditional TALSPEAK process is replaced by the extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[[EHP]). In addition, the aqueous phase complexant and buffer used in traditional TALSPEAK is replaced with the combination of N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA) and citric acid. In order to evaluate the possible impacts of gamma radiolysis upon the efficacy of the Advanced TALSPEAK flowsheet, aqueous and organic phases corresponding to the extraction section of the proposed flowsheet were irradiated in the INL test loop under an ambient atmosphere.

The variation in the rate constants for the reaction of hydroxyl radical with different aminopolycarboxylates and carboxylic acids can account for the differences observed for the irradiation of the TALSPEAK and Advanced TALSPEAK solvent systems. The results of these studies conducted at INL, led INL researchers to conclude that the scarcity of values of rate constants for the reaction of hydroxyl radical with the components of the Advanced TALSPEAK process chemistry was severely limiting the interpretation of the results of radiolysis studies performed at the INL. In this work, the rate of reaction of hydroxyl radical with citric acid at several pH values was measured using a competitive pulse radiolysis technique. The results reported here demonstrate the importance of obtaining hydroxyl radical reaction rate data for the conditions that closely resemble actual solution conditions expected to be used in an actual solvent extraction process.

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