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Abstract
The stable complexant arising from the oxidative degradation of HEDTA in synthetic Hanford high-level waste has been determined to be ethylenediaminetriacetate (ED3A). The lab work done and evidence found to identify ED3A as the HEDTA decomposition product are described.

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INTRODUCTION

Slurry growth phenomena have been observed in the Hanford high-level waste (HLW) tanks since 1977. Early laboratory studies of slurry growth revealed that the complexant HEDTA (N-(2-hydroxyethyl)ethylenediaminetriacetate) undergoes oxidative degradation under conditions available in HLW to form a relatively stable species capable of complexing ferric iron (Ref. 1). The complexant EDTA (ethylenediaminetetraacetate), also present in HLW, was found to be stable under similar conditions. Subsequent experiments conducted by Mike Jansky have shown glycolate to react in synthetic HLW but citrate to be stable. The components Na_3HEDTA, Na_4EDTA, sodium glycolate and sodium citrate are the major original contributors to the organic carbon inventory of Hanford HLW.

The identity of the stable HEDTA decomposition product is of interest in considering future waste processing and disposal operations due to its potential ability to form complexes with hazardous radioelements and its demonstrated stability to further degradation. Consequently, studies were undertaken to separate and identify this species. The HEDTA product complexant species was found to be ethylenediaminetriacetate (ED3A). The work done and evidence found to identify ED3A as the HEDTA decomposition product are described in this report. A brief discussion of ED3A chemistry and suggested future work also is presented.

EXPERIMENTAL

In Reference 1, HEDTA was shown to degrade following first order kinetics with respect to HEDTA and $NaAlO_2$. Sodium nitrite and/or nitrate were required for the reaction to proceed at a significant rate -- rates were faster with $NaNO_2$ than with $NaNO_3$. Also, the reaction rate went through a maximum with increasing NaOH concentration implying that a specific aluminum-HEDTA-hydroxide reactive intermediate was formed. The reaction had an Arrhenius temperature dependence in the range 60-120°C which implied that the reaction mechanism was unchanged in that span. The reaction rate roughly doubled with each 10°C temperature rise. At 120°C, HEDTA had a half-life of $\sim$100 hours in a simulated HLW slurry.

With the above information as a basis, a set of experimental reaction conditions were selected with the object of converting essentially all the starting HEDTA material to decomposition product in order to simplify product identification. A reaction mixture, of the composition shown in Table 1, was prepared using reagent grade chemicals and distilled water. Sodium aluminate, unavailable itself in reagent grade, was prepared using equimolar quantities of reagent grade NaOH and $Al(OH)_3$. The reaction mixture was soluble at the 100-120°C temperatures used in preparation. Crystals of $NaNO_2$ appeared upon cooling the mixture to room temperature.

A Parr Model 4749 acid digestion bomb was used as the reaction vessel in this study. Approximately 15 mL of the reaction mixture was introduced to the Parr bomb, the bomb placed in a thermostatted convection oven set at 150°C and the mixture allowed to react for two weeks. The Parr acid digestion bomb consisted of a thick-walled, high-density capped Teflon liner fit snugly into a

TABLE 1

Composition of Reaction Mixture

Component	Concentration (M)
NaOH	1.5
$NaAlO_2$	2.3
$NaNO_2$	4.0
Na_3HEDTA	1.0

stainless steel screw capped sleeve. The ability to seal the reactants in the bomb allowed the reaction to proceed about 30°C above atmospheric boiling temperatures and hastened the reaction rate about ten-fold.

Following two weeks' reaction time, the bomb was removed from the oven, allowed to cool and then opened. The product mixture was a viscous, amber liquid with a small amount of white solids and had a strong ammonia odor. The product mixture was transferred to a 125 mL flask and stirred vigorously while concentrated HNO_3 was added dropwise. Acid addition continued until the pH reached about 7, thus precipitating aluminum as aluminum hydroxide. Dense white fumes (NH_4NO_3?) were evolved while the HNO_3 was added. Only a small amount of brown NO_x fumes were evident, however, indicating the nitrite concentration had been diminished substantially.

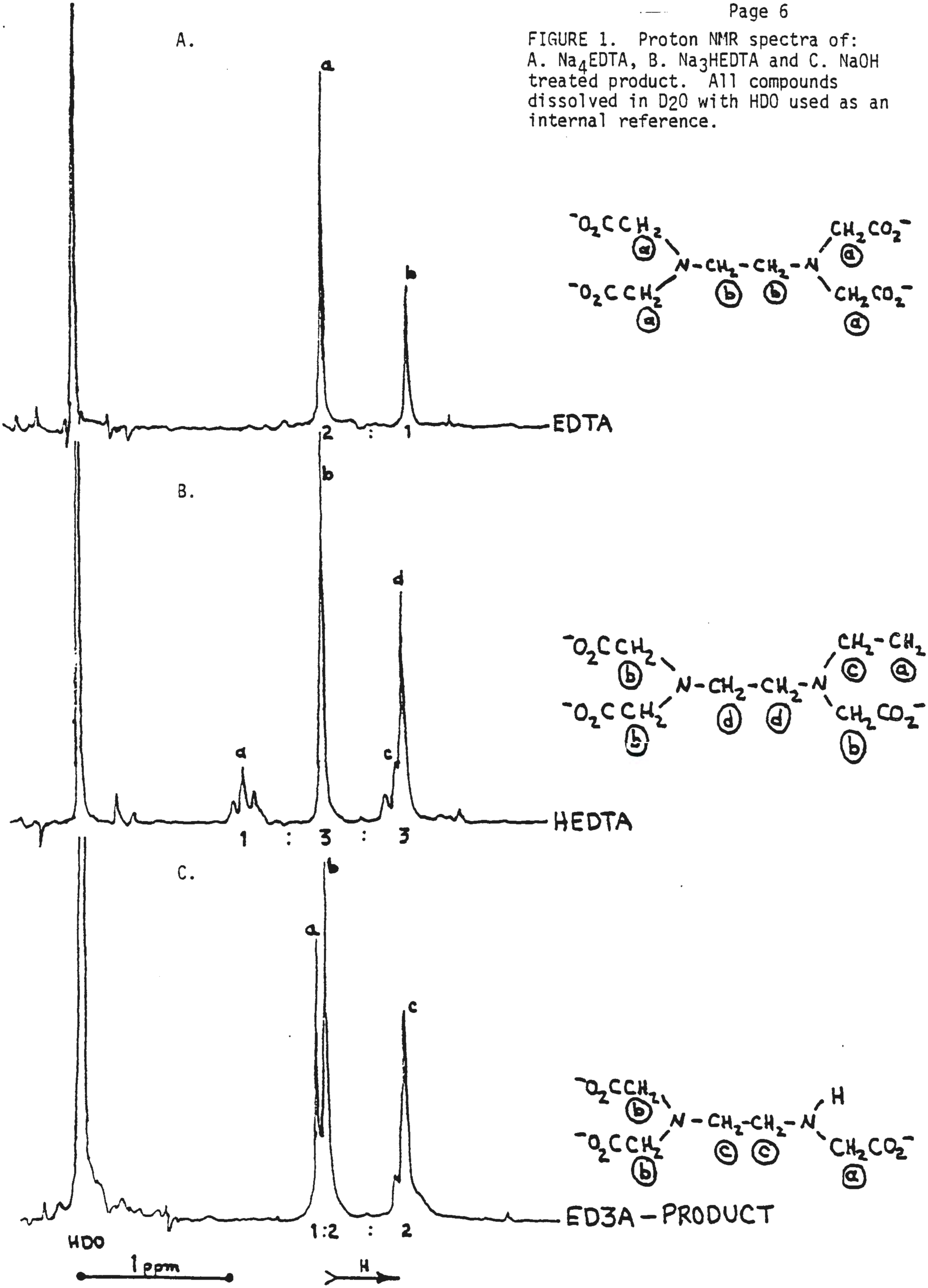
The precipitated aluminum solids were washed with several portions of water and the amber-colored water soluble fraction composited and centrifuged. The supernatant solution was transferred to a vacuum flask and the volume of the solution reduced to about 5 mL by drawing filtered air at room temperature over the solution. The resulting solution was passed through a 30 cm long column containing 40-60 mesh silica gel. The product was eluted from the column with distilled water and several portions taken. The bulk of the amber solution eluted over about 4 to 8 column volumes. The amber solution fraction was evaporated to near dryness in a vacuum flask, as described above. The flask was placed such that the bottom was slightly off horizontal. By this placement, a fractional crystallization of the product was effected and pale yellow crystals of organic product plated out on the high side of the flask bottom. Resinous, uncrystallized amber colored product collected on the low side of the flask together with cubic white crystals; presumably, the white crystals were $NaNO_3$.

The gummy organic crystals were scraped from the high side of the flask bottom. A portion was dissolved in a small quantity of distilled water (the crystals were freely soluble) and several pellets of NaOH added. The solution was heated until all NaOH dissolved. The solution was heated further to drive off excess water.

Deuterium oxide (D_2O) solutions of the original crystals and the NaOH treated crystals were analyzed by proton nuclear magnetic resonance (NMR) spectrometry. Deuterium oxide solutions of Na_3HEDTA and Na_4EDTA also were analyzed by NMR and were used for reference in making peak assignments.

The NMR spectra of Na_4EDTA, Na_3HEDTA and the NaOH treated product are reproduced in Figure 1. The proton resonance from HDO was present in all spectra and served as an internal standard for chemical shift. The product spectrum showed two peaks, with a 2:1 integrated peak ratio, in the region of the field associated with the acetate group proton resonances found in EDTA and HEDTA. A singlet, with a small peak slightly downfield and having a relative intensity of 2, was found in the region associated with the ethylene singlets of EDTA and HEDTA. The NMR evidence, therefore, was consistent with the product being ethylenediaminetriacetate (ED3A). The structure of ED3A is given in Figure 1. Assignment of the product's NMR spectrum to ED3A was confirmed by NMR spectral data for ED3A given in the literature (Ref. 2). The small peak downfield of

FIGURE 1. Proton NMR spectra of: A. Na_4EDTA, B. Na_3HEDTA and C. NaOH treated product. All compounds dissolved in D_2O with HDO used as an internal reference.

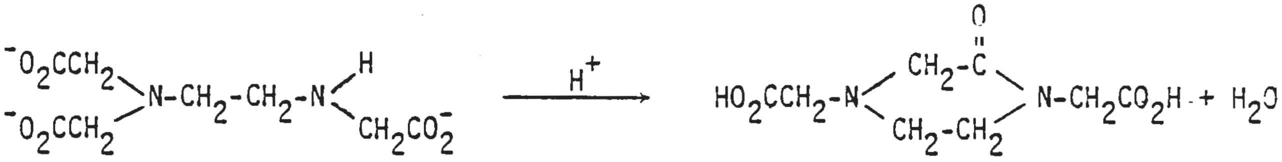


the ethylene peak in ED3A may have been due to unreacted HEDTA or to an intermediate compound.

The NMR spectrum of the original crystals (dried from solution of pH ∿7) was very complex with multiple peaks lying between the HDO peak and the field associated with acetate group protons.

DISCUSSION

The compound ED3A has been identified as an impurity in the manufacture of both EDTA and, to a lesser extent, HEDTA. Efforts to synthesize ED3A, or to separate it from EDTA, however, were unsuccessful until recently. The first separation of ED3A in the form of Co(III) complexes, occurred in 1969 (Ref. 3). Shortly thereafter, separation of ED3A as its acidified, cyclized lactam was accomplished (Ref. 4). The species ED3A will cyclize slowly upon acidification to form the lactam 2-oxo-1,4-piperazine diacetic acid (H_2OPD), as shown below:



ED3A

H_2OPD

The protons of the acetate functions of H_2OPD are acidic with $pK_1 = 2.95$ and $pK_2 = 5.85$ (Ref. 4). The lactam H_2OPD will hydrolyze in heated strong NaOH solutions and revert to ED3A (Ref. 2, 4). Thus, the HEDTA product, as crystallized from pH 7 solution, probably was a mixture of di- and monosodium salts of OPD. A complex NMR spectrum would result from such a mixture. Treatment of the pH 7 product with NaOH and heat hydrolyzed the lactam to ED3A.

The mechanism of conversion of HEDTA to ED3A in HLW has not been deduced. However, studies of the analogous Fe(III)-catalyzed oxidation of EDTA to form ED3A stoichiometrically in aqueous solutions up to pH 9.3 and above 100°C have been reported (Ref. 2). These studies showed the reaction kinetically first-order with respect to Fe(III), the reactive intermediate to be Fe(OH) EDTA and the activation energy to be 28.6 kcal/mol. The Fe(III) catalyst was reduced to Fe(II) in the EDTA reaction but could be oxidized by O_2 to Fe(III) to complete the catalytic cycle. In comparison, the oxidation of HEDTA in HLW was found to be first order in aluminum concentration and an aluminum-HEDTA-hydroxide intermediate was postulated. A reaction activation energy of 24.5 kcal/mol was found for HEDTA oxidation. Nitrate and nitrite were the HEDTA oxidants and molecular oxygen was consumed in some reaction mixtures (Ref. 1).

The authors of the Fe(III)-EDTA study postulated formaldehyde, glyoxylate ($CHOCO_2^-$) and bicarbonate as the possible reaction fragments from EDTA cleavage but no products were identified. Likewise, no carbon-bearing product fragments from HEDTA oxidation in HLW other than ED3A were identified in either the current or earlier studies. Oxalate also is a possible reaction product.

The HEDTA reaction product, ED3A, should form strong complexes with metal ions in solution. However, a 1974 compilation of metal-amino acid ligand stability constants had no data for ED3A (Ref. 5). A more exhaustive literature search for ED3A formation constant data would be useful to determine the effects ED3A might have on radionuclide chemistry in the Hanford HLW.

Further tests are necessary to determine the mechanism of HEDTA decomposition; specifically, the roles of nitrite, nitrate and oxygen in the oxidation. The presence of ED3A in genuine HLW also should be confirmed as well as the identity of the minor fragments.

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