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Thermal Stability of Ethylenedinitrilotetraacetic Acid and Its Salts

Part 2 - Rate of Decomposition in Aqueous Solution Determined by NMR Techniques

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PREVIOUS REPORT IN THIS SERIES

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ABSTRACT

To prevent pitting and scaling in marine boilers, tetralithium ethylenedinitrilotetraacetate has been proposed as a boiler-water additive. Although the sodium salts of ethylenedinitrilotetraacetic acid have been successful in reducing scale formation in various low, medium, and high-pressure utility boilers, the thermal stability of the ethylenedinitrilotetraacetate anion ($EDTA^{4-}$) has not been thoroughly investigated. Consequently, the rate and mechanism of the thermal decomposition of $EDTA^{4-}$ salts in solution were studied using nuclear magnetic resonance (nmr) techniques.

Aqueous and deuterium oxide solutions of ethylenedinitrilotetraacetic acid (H_4EDTA), disodium ethylenedinitrilotetraacetate (Na_2H_2EDTA), and tetralithium ethylenedinitrilotetraacetate (Li_4EDTA) were heated at 200°C in sealed nmr tubes for periods ranging from 1 hr to over 200 hr. Periodic examination of the contents using proton nmr showed that in all solutions the $EDTA^{4-}$ decomposed rapidly and in the solution order $H_4EDTA > Na_2H_2EDTA > Li_4EDTA$. Approximate rates for the degradation processes have been determined. The longest half-life, that for 0.1M Li_4EDTA solution, is approximately 13 hr at 200°C. In view of these results, the identity of the species which prevent scale formation and which act as a corrosion inhibitor in boiler water at high temperatures is obviously open to question.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

NRL Problems C04-04 and C07-04
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THERMAL STABILITY OF ETHYLENEDINITRILOTETRAACETIC ACID AND ITS SALTS

PART 2 - RATE OF DECOMPOSITION IN AQUEOUS SOLUTION DETERMINED BY NMR TECHNIQUES

INTRODUCTION

To reduce corrosion and pitting of boiler-tube metal in 1200-psi marine boilers, Bloom, et al. (1,2), suggested lithium hydroxide in lieu of sodium hydroxide in the low-phosphate (10 to 25 ppm PO_4^{3-}) water-control treatment. However, when the lithium hydroxide-phosphate system was tested, Bolander (3) reported that excessively high pH values were obtained, the phosphate was rapidly consumed, and a harmful insulating film (possibly Li_3PO_4) was formed on the heat-transfer surface in the boiler. Since lithium hydroxide exhibits superior ability to prevent pitting of boiler-tube metal, agents other than phosphate were sought to prevent scale formation, which arises from iron, calcium, and magnesium ions unavoidably present in the boiler makeup water.

From the standpoint of the prevention of boiler-wall pitting and corrosion, tests have indicated that lithium hydroxide in combination with an organic chelating agent, ethylenedinitrilotetraacetate ion ($EDTA^{4-}$), is preferable to the low-phosphate water-control treatment presently being used by the Navy (4,5). One of the most significant steps in the prevention of caustic corrosion in boilers is the elimination of internal deposits (6,7). $EDTA^{4-}$ not only controls the hardness of the makeup water but also prevents the formation of iron-based sludge and other deposits on the internal heat-transfer surfaces. The chelating agent effectively maintains iron, calcium, and magnesium ions in a soluble form in the boiler water and prevents the formation of precipitates. In the presence of $EDTA^{4-}$, a passive magnetite film appears to form on the boiler-tube metal which inhibits further corrosion.

Ethylenedinitrilotetraacetic acid (H_4EDTA) and its salts have been tested in utility boilers as cleaners, scale preventers, and corrosion inhibitors (8-12). The general properties of $EDTA^{4-}$ chelates and the thermal stability of H_4EDTA and its salts in solution and in the solid state have been reviewed recently (13,14).

Metal corrosion by $EDTA^{4-}$ and inactivation of the chelating ability of $EDTA^{4-}$ at temperatures of 149°C (300°F) and above have been reported (8,11,12). Merriman (8a) and Lux (12) report a drastic effect of oxygen on the corrosion rate of metals in the presence of $EDTA^{4-}$. In some tests the apparent dangers of oxygen in the presence of $EDTA^{4-}$ necessitated protecting the boiler during off-line periods by such means as pressurizing the boiler with 5 psi of nitrogen. Jacklin (11) reported a sharp drop in the scale prevention action of $EDTA^{4-}$ between 217°C (422°F) and 231°C (448°F) in the presence of dissolved oxygen, but some preventive action was retained at the higher temperature. Tests on $EDTA^{4-}$ at 271°C (520°F) with 1 ppm of dissolved oxygen and 10 ppm hardness in the feedwater showed that the chelating agent acted as an oxygen scavenger, but the efficiency of scale prevention was greatly decreased.

Temperatures near 177°C (350°F) appear to activate dissolved oxygen and cause a degradation of $EDTA^{4-}$. The degradation is reported to be incomplete. Edwards and Merriman (13) report that one part of oxygen equivalent causes 50 to 100 parts of $EDTA^{4-}$ to be nearly worthless as far as preventing deposits in the boiler. When oxygen-free water

is used, free $EDTA^{4-}$ and metal complexes are reported to be stable to temperatures of 251°C (484°F) for a period of 2 hr. Sodium sulfite may be added to the makeup water with $EDTA^{4-}$ to reduce the oxygen content of the boiler water and enhance the activity of the chelating agent (15). Other oxidizing agents, such as peroxide, hypochlorite, permanganate, thiosulfate, ceric, and vanadate ions, will also degrade $EDTA^{4-}$ by oxidation (13, 16). The products of the degradation have not been thoroughly studied.

Although laboratory tests have been conducted to determine the temperature at which $EDTA^{4-}$ can be used in boilers without thermal decomposition of the chelating agent, complete experimental details and results are not available (13). In the absence of oxygen, Edwards and Merriman (13) report that $EDTA^{4-}$ appears to be stable to at least 204°C (400°F), and solutions containing 100 to 200 ppm $EDTA^{4-}$ gave indications of complete stability of the "free chelate" (metal chelate) up to 260°C (500°F).

Steam purity should not be affected because of the nonvolatile nature of the organic chelating agent; however, thermal degradation of $EDTA^{4-}$ should be accompanied by increased conductivity and changed pH of the steam if the degradation products are volatile. No such changes have been reported nor has the nitrogen content of the steam changed with varying amounts of added organic chelating agent (13). Although the experimental details and detailed results were not given, Edwards and Merriman (13) report that careful analytical checks on feedwater, boiler water, and steam purity also indicated no measurable decomposition of $EDTA^{4-}$ at the operating drum temperature of 231°C (448°F). For best results, Na_4EDTA solutions are injected into the boiler feedline to completely chelate the hardness ions at the lower temperatures in the feedline (about 135°C, 275°F), thus subjecting only the more stable chelates to the high drum temperatures (8,10,13). The initial feed rate of Na_4EDTA should be set at a level which is just sufficient to completely chelate the hardness going in with the feedwater; "unchelated" $EDTA^{4-}$ should be maintained at 10 to 20 ppm (13).

The utility of the lithium-ethylenedinitrilotetraacetate water treatment must be verified by testing in marine boilers. To help expedite Navy use of the new water treatment, NRL has initiated a program to study (a) the stability of the organic chelating agent, $EDTA^{4-}$, and its coordination compounds in aqueous solutions at high temperatures; (b) the rate of organic chelate decomposition in aqueous solutions at high temperatures; (c) the identification of thermal decomposition products; (d) the effectiveness of organic chelating agents and any of their thermal decomposition products to complex iron, calcium, and magnesium in solutions at high temperatures; (e) the analytical methods to be used aboard ship for determining residual concentrations in boiler water for specific organic chelating agents; and (f) the possibility of using other chelating agents in lieu of $EDTA^{4-}$ in the lithium hydroxide water treatment.

Analytical methods reported for the estimation of residual $EDTA^{4-}$ in boiler water fail to take into account the possible formation of new nonvolatile chelating agents through the degradation of $EDTA^{4-}$. Using nuclear magnetic resonance (nmr) techniques, which recorded the proton spectra of the organic chelating agent, we studied and report herein the rate of thermal decomposition of aqueous and deuterium oxide solutions containing H_4EDTA, disodium ethylenedinitrilotetraacetate (Na_2H_2EDTA), and tetralithium ethylenedinitrilotetraacetate (Li_4EDTA).

EXPERIMENTAL PROCEDURES

Reagents

H_4EDTA (Fisher-Certified reagent) and Na_2H_2EDTA (Baker-Analyzed reagent) were used without further purification. Li_4EDTA was prepared by reacting the acid with lithium carbonate (17). Distilled water and deuterium oxide (Bio-Rad Laboratories, 99.84 mole-% D_2O) were used as solvents to prepare the appropriate solutions.

Sample Preparation

A 0.25M stock solution of Na_2H_2EDTA in H_2O was prepared, and the required amounts transferred to an nmr-tube. All other solutions, H_2O and D_2O, were prepared by dissolving in an nmr tube the appropriate quantity of solid in 1 ml of solvent. The acid was not soluble in H_2O or D_2O, and only 0.5 ml of the mixture was prepared. For solutions, one-half of the liquid was transferred to a second nmr tube and freeze-thaw degassed four times under reduced pressure (10^{-3} to 10^{-4} torr); finally, the solution or mixture was sealed under reduced pressure. About 15 μl of H_2O was added to the D_2O solutions to serve as a locking signal for the nmr spectrometer. The unsealed solution was retained as a standard solution.

Procedure

The sealed nmr tube was placed in an 8-in. length of 1/4-in. steel pipe capped at each end. The tubes and protective jacket were heated in an oven set at 200°C ± 5°C; the length of heating period designates the time the tube was in the oven. The tube was allowed to cool 45 min before it was removed from the protective jacket. The nmr spectrum of a sample was determined initially and following each period of heating.

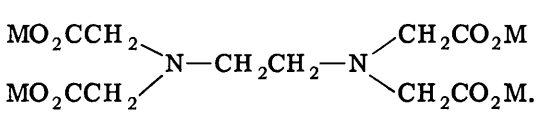
Nmr Data

Nmr spectra were recorded using a Varian HA-100 spectrometer, operating in the field-sweep mode. The water peak was used as the locking signal. As much as practicable, identical instrument settings were used for a given sample; the control sample was used to reset any variations in peak intensities. This facilitated quantitative measurement of spectral changes. Electronic integration could not be employed because of the close spacing between peaks and the proximity to the lock signal. Consequently, signal heights were measured from the recordings. Peak positions were measured to ±0.1 Hz with a frequency counter.

RESULTS

Nmr Spectrum of M_4EDTA (M = H or monovalent metal ion)

The proton nmr spectrum of M_4EDTA consists of two lines, in an intensity ratio of 2:1, which correspond to the two kinds of protons in the molecule–those situated on the carbon atom α to the carbonyl group (eight per molecule) and those situated on the carbon atoms between the two nitrogens (four per molecule) (Fig. 1a):



If M is H, the rapid exchange of this acidic proton averages its signal with that of the bulk-water solvent. Since the spectrometer is operated in such a way that the locking signal is derived from the protons in the bulk-water peak, information on the carboxylic acid protons is not obtainable.

The symmetry and configuration of the M_4EDTA molecule are such that there is no observable spin coupling between protons. The nitrogen atoms are presumably relaxing (changing spin states) rapidly due to quadrupolar effects, thus washing out nitrogen-proton spin coupling.

Four cycles of the freeze-pump-thaw degassing were assumed sufficient to remove traces of dissolved oxygen from the solutions sealed in the nmr tubes. By simulating the degassing on 25 ml of distilled water, we found approximately 0.08 ppm of oxygen. However, this quantity of oxygen is attributed to gas absorbed during sample handling in the gas chromatographic method used to determine dissolved oxygen (18,19). Consequently, the thermal decompositions may be considered as taking place in the absence of dissolved oxygen.

Solution Decomposition of Na_2H_2EDTA

In H_2O – Since 0.18M Na_2H_2EDTA was the first substance for which solution thermal decomposition was attempted, mild temperatures and short exposure periods were employed initially. After 16 hr at 125°C* and 16 hr at 150°C, no observable changes in the nmr spectrum occurred compared to the spectrum of an unheated sample (Fig. 1a). It appears that 200°C is about the lowest temperature at which decomposition proceeds at any significant rate. After 1.5 hr at 200°C, gross changes in the spectrum were apparent (Fig. 1b). The signal at 89 Hz had decreased in relative intensity, and a new signal appeared slightly upfield from it at 92 Hz. In addition, a pair of multiplets centered at 88 and 137 Hz appeared. As heating proceeded, the signal at 89 Hz decreased further in intensity, while the signals centered at 92, 88, and 137 Hz continued to grow. After 3.5 hr at 200°C (Fig. 1c) a signal appeared at 115 Hz, slightly upfield from the 113-Hz peak. The significant changes in the spectrum on additional heating to 9.5 hr involve the 89 and 113 Hz signals, which decreased in intensity and moved to 112 and 144 Hz, respectively, before disappearing (Fig. 1d). After much longer heating times (up to 320 hr), additional signals at higher fields (ca. 190 and 207 Hz) were noticeable.

In D_2O – A sample of Na_2H_2EDTA was run in D_2O under the same conditions as the aqueous solution. The nmr spectrum of the unheated solution is shown in Fig. 2a. After 1 hr at 200°C, the signal at 87 Hz had completely disappeared, and the signal at 109 Hz had decreased in amplitude significantly (Fig. 2b). The multiplets centered at 88 and 137 Hz were comparable in size and appearance to those of the sample in H_2O solution after 1.5 hr at 200° (Fig. 1b). Additional heating to 5 hr reduced the size of the 109-Hz signal, while it also gradually moved upfield (Fig. 2c). Although the multiplets centered at 88 and 137 Hz initially increased in intensity, the signals showed no loss in intensity when heated from 10 up to 20 hr at 200°C (Figs. 2d and 2e, respectively). Though it is not possible to make a quantitative assessment, it appears that the intensities of the 88 and 137 Hz multiplets in the D_2O solution lagged behind those in the aqueous solution and that their rate of growth in the D_2O solution lessened as the amount of deuteration of the signal at 109 Hz increased.

Solution Decomposition of Li_4EDTA

The Li_4EDTA decomposition was followed at two concentrations, 0.26M and 0.1M, with similar results observed. The following description and Fig. 3 refer to the 0.26M solution.

The spectrum of 0.26M Li_4EDTA is similar to that of Na_2H_2EDTA solution (Fig. 1a) in that there are two singlets of a 2:1 intensity ratio. However, the peak positions are shifted to higher field and are more widely separated in the case of the lithium compound (Fig. 3a).

In H_2O – The thermal decomposition of Li_4EDTA in H_2O proceeds more slowly than that of Na_2H_2EDTA in H_2O, and the products are different. Reference to Fig. 3b shows

*Refers to oven temperature.

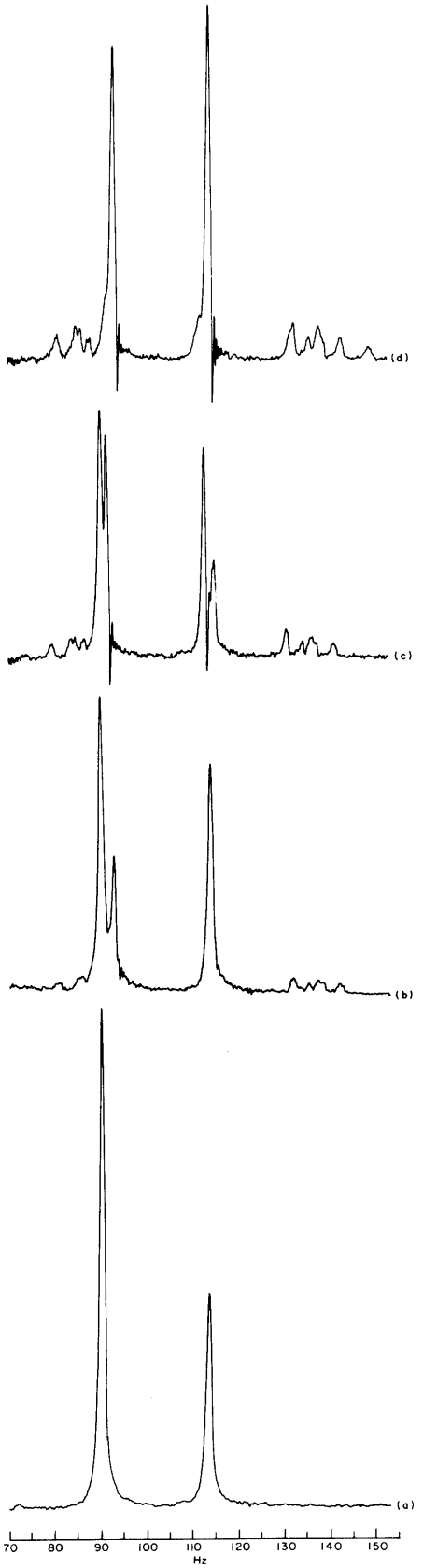


Fig. 1 - Nmr spectra of a 0.18M aqueous solution of $Na_2H_2EDTA \cdot 2H_2O$ sealed under reduced pressure: (a) Unheated, (b) heated 1.5 hr at 200°C, (c) heated 3.5 hr at 200°C, and (d) heated 9.5 hr at 200°C

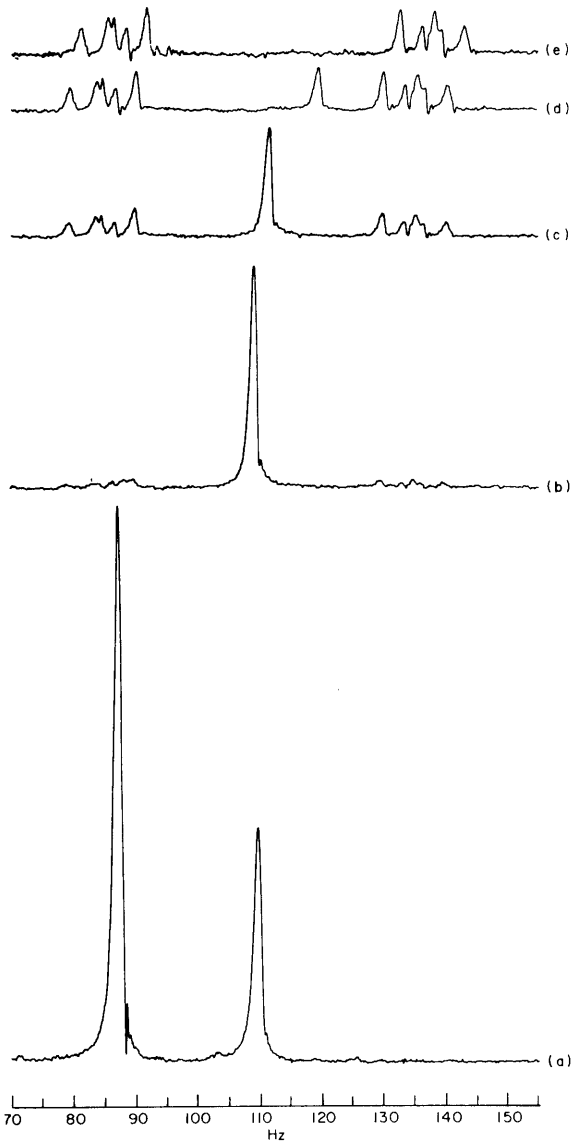


Fig. 2 - Nmr spectra of 0.17M deuterium oxide solution of $Na_2H_2EDTA \cdot 2H_2O$ sealed under reduced pressure: (a) Unheated, (b) heated 1 hr at 200°C, (c) heated 5 hr at 200°C, (d) heated 10 hr at 200°C, and (e) heated 20 hr at 200°C

that after 5 hr at 210°, a singlet has appeared at 155 Hz; after 45 hr a singlet has appeared at 161 Hz and a triplet at 120 Hz, and what looks to be a pair of satellites has appeared around the 213-Hz signal (Fig. 3c). This pair of satellites is undoubtedly part of a triplet similar to the one at 120 Hz but whose central component accidentally overlies the 213-Hz peak. The singlet at 161 Hz is seen to grow as the decomposition proceeds. With additional heating up to 209.5 hr, the triplets centered at 120 and 213 Hz and singlets at 151 and 161 Hz continue to grow, while the original signals at 159 and 213 Hz decrease in intensity (Figs. 3d and 3e).

In D_2O – Runs of 0.1M and 0.28M Li_4EDTA in D_2O solution reproduced the effects mentioned above, except that the peak at 158 Hz rapidly disappeared, and the 155 and 160 Hz peaks were not observed (Figs. 4a to 4d).

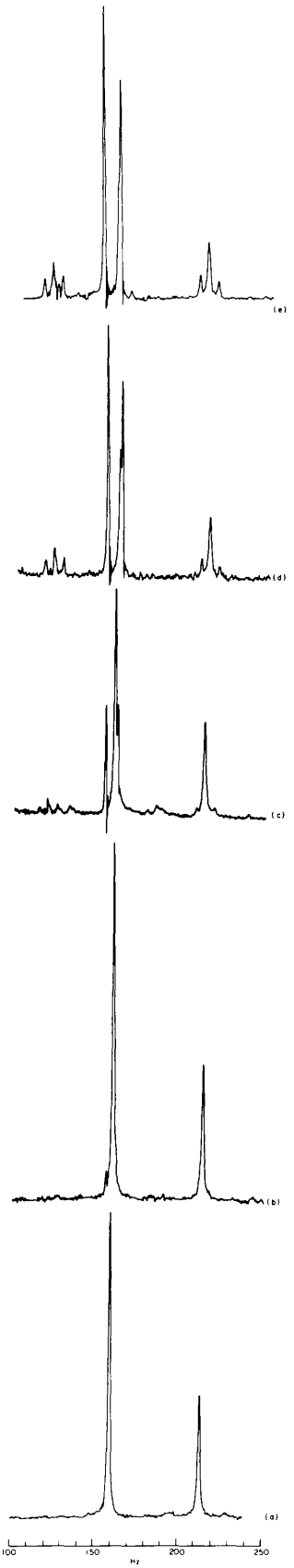


Fig. 3 - Nmr spectra of 0.26M aqueous solution of Li_4EDTA sealed under reduced pressure: (a) Unheated, (b) heated 5 hr at 210°C, (c) heated 45 hr at 210°C, (d) heated 137.5 hr at 210°C, and (e) heated 209.5 hr at 210°C

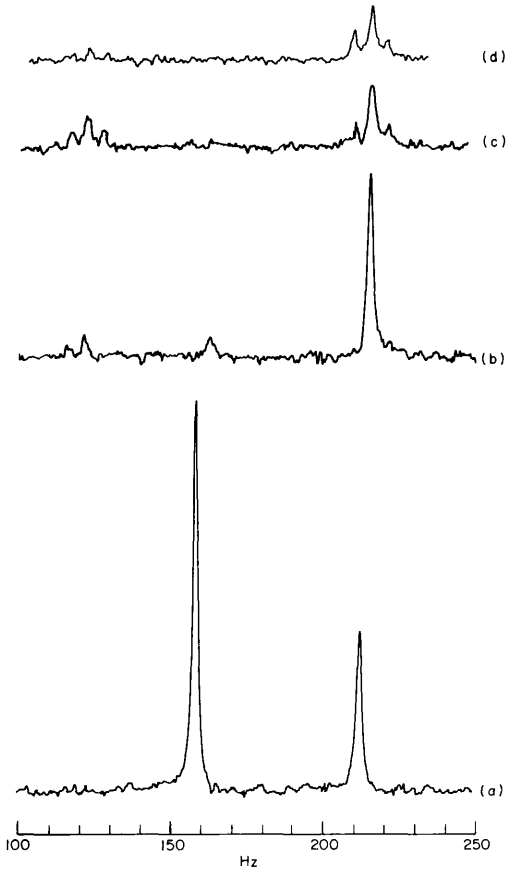


Fig. 4 - Nmr spectra of 0.28M deuterium oxide solution of Li_4EDTA sealed under reduced pressure: (a) Unheated, (b) heated 5 hr at 200°C, (c) heated 42.5 hr at 200°C, and (d) heated 154 hr at 200°C

Solution Decomposition of H_4EDTA

The results for the acid are less definitive than those for its disodium and tetralithium salts, because H_4EDTA does not dissolve in water to a sufficient extent at room temperature to be detected by nmr. However, on heating at 200°C decomposition occurs with the formation of water-soluble products. After 21 hr, it is apparent from Fig. 5a that several species are present in solution. At this point the solution was yellow-orange, and a yellow scum had appeared on the walls of the sealed tube. On further heating, some signals increased in intensity, while others decreased; however, no new peaks appeared (Fig. 5b). Soluble decomposition products formed in D_2O solution had nmr peaks similar to the aqueous solutions; however, the more intense signals in the latter spectra were absent in the D_2O solution (Fig. 6).

DISCUSSION

Na_2H_2EDTA

The changes which occur in the nmr spectrum of Na_2H_2EDTA in oxygen-free aqueous solution at 200°C are consistent with its transformation into different species. It appears that the decrease in intensity of the 89-Hz signal corresponds to the loss of $-CH_2COOM$ or $-CH_2COO-$ groups. The main product (Fig. 1d) which is formed has singlet signals at 92 Hz and 113 Hz, with intensities in the ratio 1:1, leading to the conclusion that it is most likely $MO_2CCH_2NHCH_2CH_2NHCH_2CO_2M$. The amine hydrogens, being exchangeable, are presumably averaged in with the H_2O peak. The multiplets centered at 88 and 137 Hz

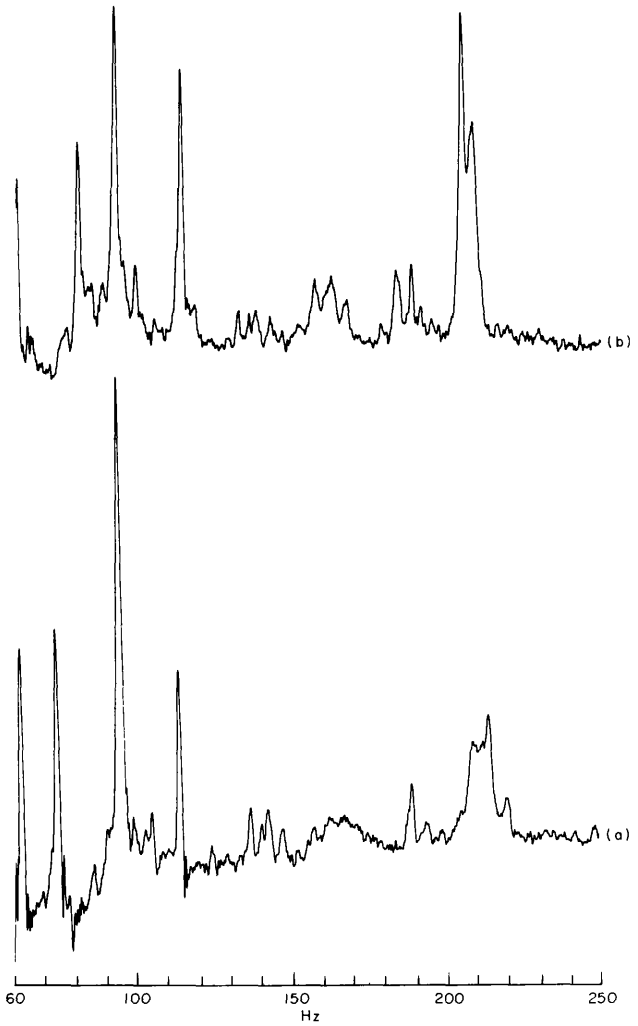


Fig. 5 - Nmr spectra of soluble decomposition products from aqueous H_4EDTA solutions heated at 200°C sealed under reduced pressure: (a) 21 hr, and (b) 80 hr

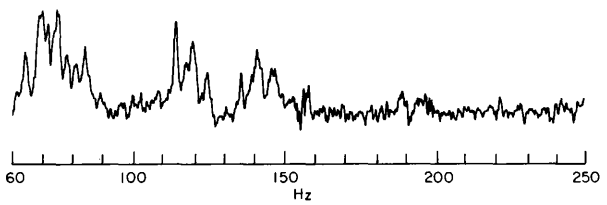


Fig. 6 - Nmr spectra of soluble decomposition products from deuterium oxide-H_4EDTA solutions heated 15 hr at 200°C sealed under reduced pressure

are due to a second-product molecule, which has nonequivalent methylene groups between the nitrogens. However, the splitting patterns are more complex than the simple pair of triplets which would be expected from a species such as $H_2N—CH_2CH_2—N—(CH_2CO_2M)_2$ and thus may be indicative of a more profound change in structure.

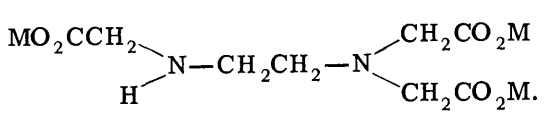
A second, slower degradation results in the formation of more complex products. Whether these arise from the decomposition of the symmetrical or unsymmetrical species cannot be determined from the present data.

The D_2O results confirm the idea that the signals in the 89 to 92 Hz region of the spectrum arise from the protons of residual $—CH_2CO_2M$ groups, since such protons are expected to be readily exchangeable. The $>N—CH_2CH_2—N<$ type protons exchange much more slowly. Similarly, the multiplets centered at 88 and 137 Hz must not be $—CH_2CO_2M$ type protons, since they persist in the D_2O sample. Also, since they do not exchange after 20 hr, as do the signals at 113 Hz, they presumably are not of the $>N—CH_2CH_2—N<$ type.

By following the peak heights of the disappearing and appearing signals of the H_2O sample as a function of time, it was possible to approximate the kinetics of the decomposition of Na_2H_2EDTA as second order. At the concentrations employed (0.18M), one-half of the Na_2H_2EDTA had decomposed after 2.7 hr at 200°C. The nature of our experimental procedure, with the lack of control over heating and cooling times, does not allow for more rigorous treatment of the rate results.

Li_4EDTA

Identification of the degradation products of Li_4EDTA is not as straightforward as was the case with Na_2H_2EDTA. The triplets centered at 120 and 213 Hz and the sharp singlets at 151 and 161 Hz apparently constitute the spectrum (or spectra) of the product(s) (Fig. 3e). The D_2O results show that the signals from 155 to 161 Hz belong to the protons of the $—CH_2COOM$ fragment, since they readily exchange. The narrower line width (sharpness) of the 156 and 161 Hz signals relative to the other lines of the spectrum precludes a meaningful comparison of peak heights, which would allow a calculation of the number of protons of each kind. However, it does appear that the ratio of 151 to 161 Hz signals is about 2:1 and that the ratio of peak area of the two triplets to that of the 151-Hz signal is approximately 1:1. If such were indeed the case, then the indicated degradation product is



While it is reasonable, such a structure for the degradation product is, with the information at hand, a speculative one.

At 200°C, the decomposition of Li_4EDTA in oxygen-free aqueous solution is relatively slow. As a consequence, the heating and cooling cycles between the heating periods of several hours represent only a small fraction of the total heating time. It therefore is reasonable to treat the degradation process quantitatively, which was not the case with the Na_2H_2EDTA solutions. The height of the $>N—CH_2CH_2—N<$ peak at 211 Hz was measured after the various heating times for the 0.1M Li_4EDTA solution. Corrections were made for the central component of the triplet, which also falls at 211 Hz. Since the spectra were measured under identical instrument conditions, the decrease in height of the peak at 211 Hz should be a measure of the rate of disappearance of Li_4EDTA. The data obtained in this way give nonlinear zero-order and first-order rate plots; however,

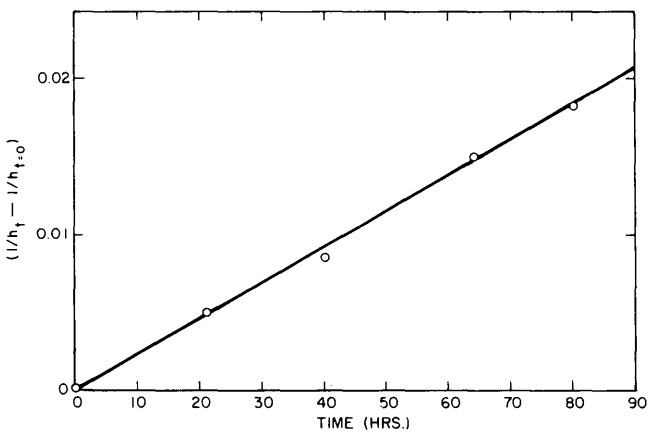


Fig. 7 - Second-order rate plot for the decomposition of 0.1M aqueous Li_4EDTA solution at 200°C

a linear plot is obtained if second-order kinetics are assumed (Fig. 7). At the initial concentration employed, one-half of the Li_4EDTA has decomposed after 13 hr at 200°C.

The initial degradation product of Li_4EDTA is relatively stable; after 302 hr at 200°C, no new signals had appeared in the nmr spectrum. Whether such a situation would prevail after longer heating times or higher temperatures is open to speculation. Nonetheless, the Li_4EDTA degradation product is obviously significantly more stable than that of Na_2H_2EDTA.

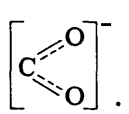
H_4EDTA

Because of the solubility problems and the abundance of nmr lines, it is not possible to determine what degradation products arise in the case of the H_4EDTA sample. However, it is certain that both the variety of products and the degree of degradation exceed those of the other two samples after a corresponding time at 200°C. Therefore, it is concluded that a solution of H_4EDTA degrades more rapidly than solutions of either Li_4EDTA or Na_2H_2EDTA.

CONCLUSIONS AND FUTURE WORK

Oxygen-free aqueous solutions of Li_4EDTA, Na_2H_2EDTA, and H_4EDTA degrade when heated to 200°C. The stability order of the solutions is $Li_4EDTA > Na_2H_2EDTA > H_4EDTA$. For the first two solutions, the degradation process was found to be second order in the concentration of $EDTA^{4-}$ salt. At the concentration levels employed (0.1 to 0.3M), the half-life is 13 hr for Li_4EDTA and about 3 hr for Na_2H_2EDTA. Because of solubility problems and the rapidity of degradation, the kinetics of the decomposition of H_4EDTA could not be determined.

The number of free carboxylate groups ($-COO^-$) in a polybasic acid depends on the pH of the solution. Initial pH values of the solutions studied were Li_4EDTA, 9.8; Na_2H_2EDTA, 4.5; and H_4EDTA, 2.8. Thus, the stability order in solution $Li_4EDTA > Na_2H_2EDTA > H_4EDTA$ may be a result of resonance stabilization of the free carboxylate ions:



Such resonance is not possible in the protonated group —COOH. Since the presence of —COOH groups appears to increase the rate of decomposition, it is possible that the acidic proton plays an active part in the degradation process, perhaps through a hydrogen-bonding mechanism.

Overriding the questions of mechanism and relative stability is the evidence that none of the compounds studied is indefinitely stable in oxygen-free aqueous solution at temperatures of 200°C and higher. Taking into account that a doubling in rate is usually observed for every 10°C increase in temperature, it is obvious that at typical Navy-boiler temperatures (316°C), the lifetime of these compounds would be short indeed.

The studies reported here relate only to a particular set of conditions. For example, what would be the effects on decomposition rates of pH and of chelation to metal ions? Are the decomposition products themselves effective chelating agents, and to what temperature are they stable? And finally, what is the mechanism of the decomposition of the $EDTA^{4-}$ salts in aqueous solution, and what are the exact products? These and other aspects of this problem are under investigation and will be the subject of further reports in this series.

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13. ABSTRACT

To prevent pitting and scaling in marine boilers, tetralithium ethylenedinitrilotetraacetate has been proposed as a boiler-water additive. Although the sodium salts of ethylenedinitrilotetraacetic acid have been successful in reducing scale formation in various low, medium, and high-pressure utility boilers, the thermal stability of the ethylenedinitrilotetraacetate anion ($EDTA^{4-}$) has not been thoroughly investigated. Consequently, the rate and mechanism of the thermal decomposition of $EDTA^{4-}$ salts in solution were studied using nuclear magnetic resonance (nmr) techniques.

Aqueous and deuterium oxide solutions of ethylenedinitrilotetraacetic acid (H_4EDTA), disodium ethylenedinitrilotetraacetate (Na_2H_2EDTA), and tetralithium ethylenedinitrilotetraacetate (Li_4EDTA) were heated at 200°C in sealed nmr tubes for periods ranging from 1 hr to over 200 hr. Periodic examination of the contents using proton nmr showed that in all solutions the $EDTA^{4-}$ decomposed rapidly and in the solution order $H_4EDTA > Na_2H_2EDTA > Li_4EDTA$. Approximate rates for the degradation processes have been determined. The longest half-life, that for 0.1M Li_4EDTA solution, is approximately 13 hr at 200°C. In view of these results, the identity of the species which prevent scale formation and which act as a corrosion inhibitor in boiler water at high temperatures is obviously open to question.

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