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Anodic Oxidation of Tetrasodium Ethylenediaminetetraacetic Acid in Alkaine Solutions (U)

by
D. T. Hobbs
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

S. N. Pakalapati
Westinghouse Savannah River Company
SC USA

B. N. Popor
Westinghouse Savannah River Company
SC USA

R. E. White
Westinghouse Savannah River Company
SC USA

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1 S. N. R. Pakalapati, Dept. of Chemical Engineering, Univ. of South Carolina
Columbia, SC 29208. Tel:(803) 777-0121 Fax:(803) 777-8265

2 B. N. Popov, Dept. of Chemical Engineering, Univ. of South Carolina
Columbia, SC 29208, Tel:(803) 777-7314 Fax:(803) 777-8265

3 R. E. White, Dept. of Chemical Engineering, Univ. of South Carolina
Columbia, SC 29208. Tel:(803) 777-3270 Fax:(803) 777-8265

4 D. T. Hobbs, Westinghouse Savannah River Company, P.O. Box 616
Aiken, SC 29802, Tel: (803) 725-2838 Fax:(803) 725-4704

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Anodic oxidation of Tetrasodium Ethylenediaminetetraacetic acid (Na_4EDTA) was studied in alkaline media using platinum electrode. Cyclic voltammetry and polarization techniques were used to obtain kinetic information. Polarization studies at different temperatures yielded activation energies of 73.0 kJ and 70.48 kJ for Na_4EDTA oxidation in NaOH solution (pH=12) at potentials 0.8 V and 0.9 V versus Hg/HgO reference electrode, respectively. Bulk electrolysis of Na_4EDTA was carried out at different pH's.

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ANODIC OXIDATION OF TETRASODIUM ETHLYENEDIAMINETETRAACETIC ACID IN ALKALINE SOLUTIONS

S. N. R. Pakalapati, B. N. Popov, R. E. White
Department of Chemical Engineering
University of South Carolina, Columbia, SC 29208
and
D. T. Hobbs
Westinghouse Savannah River Company
Savannah River Laboratory, Aiken, SC 29808

Introduction

Electrochemical oxidation is being increasingly considered in recent years as a technique to destroy organic compounds in industrial waste [1]. Johnson *et al.* [2] studied the anodic oxidation of HEDTA on platinum in acid sulfate solutions. Polarizations relationships were obtained and numerous reactions products were identified that indicated a sequential removal of acetate groups from the EDTA. The initial decarboxylation was followed by a reverse Schiff-type reaction which produced formaldehyde and the corresponding amine.

The purpose of this investigation was to determine if tetrasodium ethylenediaminetetraacetic acid (Na_4EDTA) could be oxidized on platinum in alkaline solutions and to obtain information about the electrochemical reaction kinetics necessary to model the electrochemical destruction of Na_4EDTA in alkaline solutions.

Experimental

The polarization studies were carried out in a three compartment cell. Platinum rotating disc electrode with a geometric area of 0.5 cm^2 was used as a working electrode. A standard Hg/HgO was used as a reference electrode and a platinum gauze served as an auxiliary electrode. Nitrogen was bubbled through the cell to provide an inert atmosphere. The electrolyte used was NaOH at pH's 11–14. The Na_4EDTA concentration was varied in the range between $5x10^{-3}M$ and 0.263M.

Tafel experiments and cyclic voltammograms were obtained at 25°C using Model 352 SoftCorr and Model 270 software respectively and using EG&G PAR potentiostat/galvanostat Model 273A. All polarization curves were obtained using a sweep rate of v=1mV/s.

The bulk electrolysis was carried out in a conventional electrochemical cell (400 mL capacity) using platinum working electrode with an area of 12.5 cm^2 and a platinum gauze auxiliary electrode. The current density applied was 0.16 A/cm^2.

Results and Discussion

Cyclic voltammetry. Fig. 1 shows cyclic voltammogram obtained on platinum rotating disc electrode in the absence and presence of 0.1 M Na_4EDTA and in the electrolyte which contained NaOH, pH=13. The experiment was carried out using a sweep rate of v=25 mV/s. As shown in Fig. 1, a distinct peak is observed at *ca*, –1.05 V *vs* Hg/HgO reference electrode for Na_4EDTA oxidation. The peak maximum was not found to be a linear function of the sweep rate indicating that the EDTA oxidation was not controlled by diffusion of the electroactive species from the bulk of the electrolyte.

Fig. 2 shows cyclic voltammograms obtained at pH=12 for different concentrations of Na_4EDTA in the electrolyte. As shown in Fig. 2, the current densities increase with increasing Na_4EDTA

concentration. Note that at pH=12, the oxygen evolution is almost negligible in the potential range 0.8 V through 1.4 V *vs* Hg/HgO reference electrode. The OH^- oxidation current density at 1.4 V *vs* Hg/HgO reference electrode is approximately 1 mA/cm^2 compared with Na_4EDTA anodic current density of 32 mA/cm^2.

Polarization Measurements. Fig. 3 shows potentiodynamic scans (v= 1mV/s) with and without EDTA in the electrolyte. As shown in Fig. 3, there is a linear section of the potentiodynamic curve above the rest potential for EDTA oxidation with a slope of about 200 mV/decade. The limiting current region was reached at potentials of about 1.0 V *vs* Hg/HgO reference electrode. As seen in Fig. 3, the current densities obtained in the presence and absence of Na_4EDTA in the electrolyte differ substantially, indicating the participation of Na_4EDTA in the oxidation process.

Fig. 4. shows polarization curves (v=1 mV/s) obtained at different temperatures (25°C, 30°C, 35°C, and 40 °C) for 0.263 M Na_4EDTA at pH=12. The limiting Na_4EDTA oxidation current was found to increase with temperature. Arrhenius plots for 0.263 M Na_4EDTA at pH=12 are shown in Fig. 5 for potentials, of 0.8 V and 0.9 V *vs* Hg/HgO reference electrode. The slopes of the two straight lines yielded activation energies of 73.0 kJ and 70.48 kJ, respectively.

Several qualitative conclusions can be drawn from the polarization studies: (i) Na_4EDTA concentration effect on polarization curves indicates that the EDTA species are adsorbed on the electrode surface; (ii) significant coverages are involved; (iii) because of the observed positive Na_4EDTA concentration effect, the rate determining step involves oxidation of electroactive species of Na_4EDTA. Langmuir, Temkin and Frumkin type of adsorption are considered and will be discussed with regard to the kinetic parameters associated with the rate determining step of the electron transfer.

Bulk Electrolysis. Fig. 6 shows the Na_4EDTA concentration as a function of charge passed at different pH's. It can be seen in this figure (Fig. 6) that the Na_4EDTA concentration decreases with charge passed indicating that the Na_4EDTA is being oxidized. At higher pH's, the Na_4EDTA destruction rate is lower due to the increased hydroxyl content in the electrolyte and consequently higher participation of oxygen evolution current in the overall oxidation process.

Acknowledgment

This work was supported by the Westinghouse Savannah River Company, Contract No. AA00900T, under Task No. 112.

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2. J. W. Johnson, H. W. Jiang, S. B. Hanna and W. J. James, ***J.*** *Electrochem. Soc.,* **119,** 574, (1972)

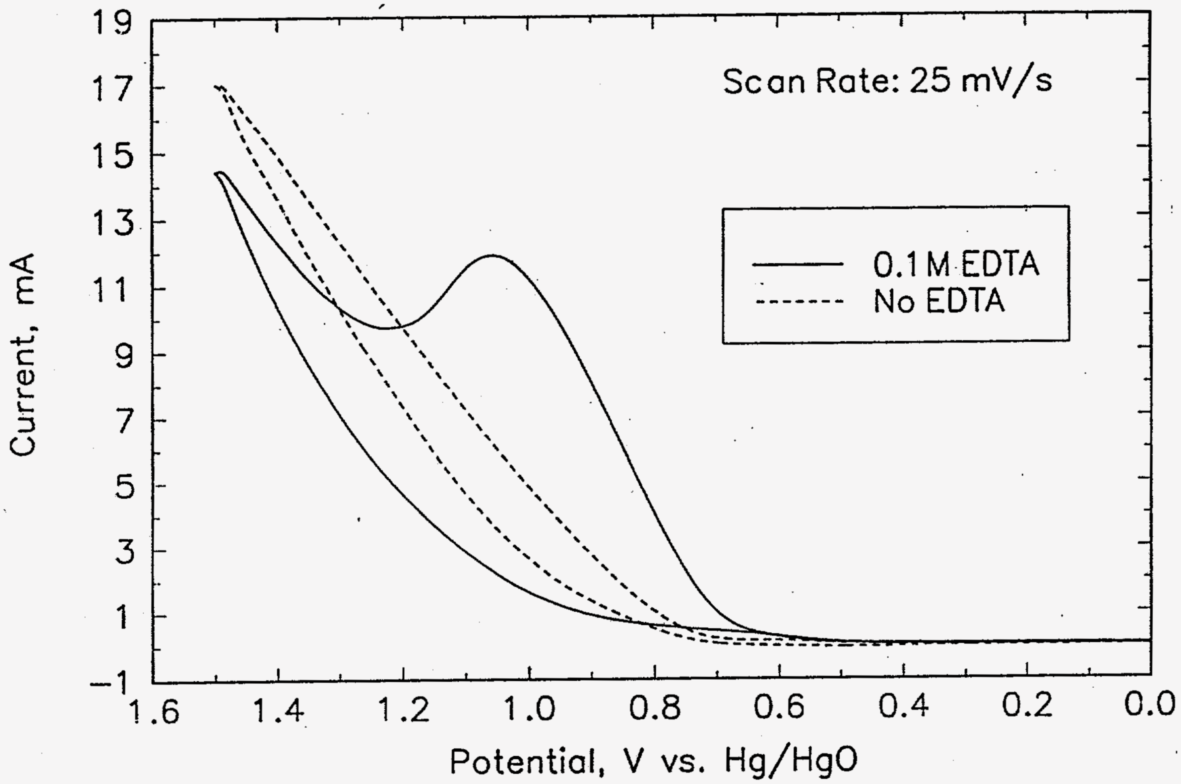

Figure 1. Cyclic voltammograms (with and without Na_4EDTA) using platinum electrode in NaOH solution (pH=13).

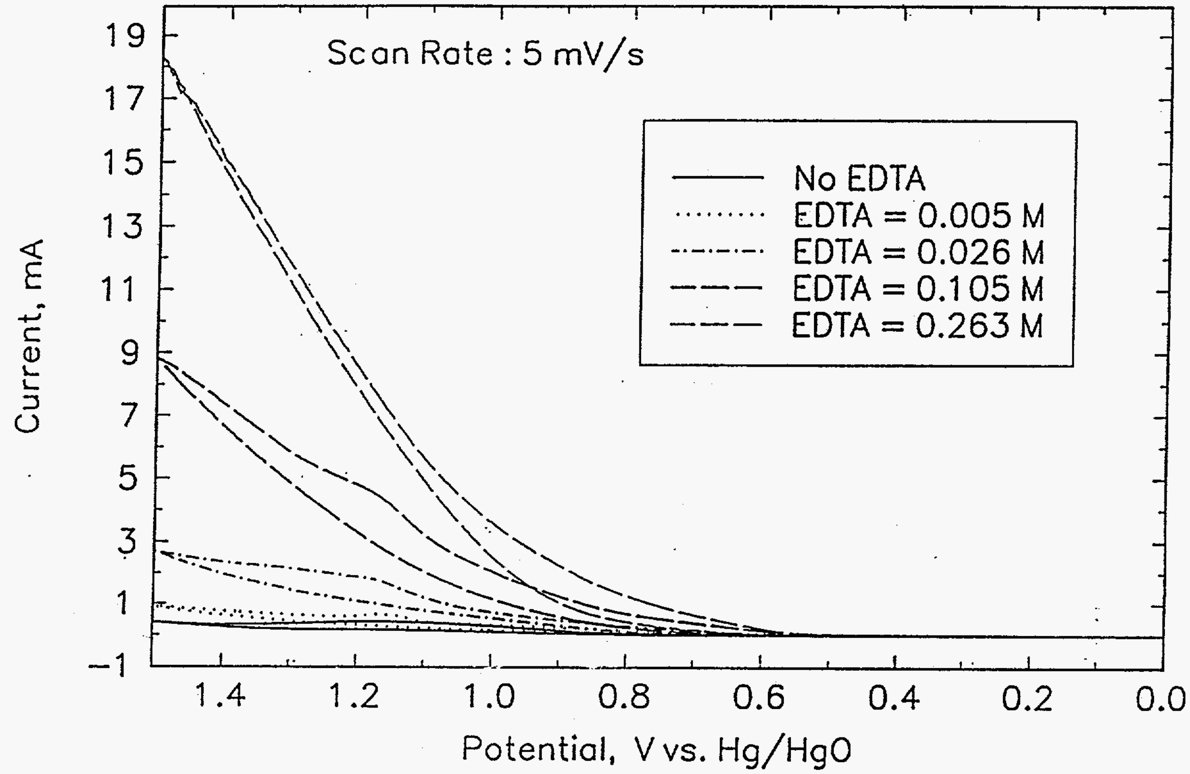

Figure 2. Cyclic voltammograms using platinum electrode in NaOH solutions with different Na_4EDTA concentration (pH=12).

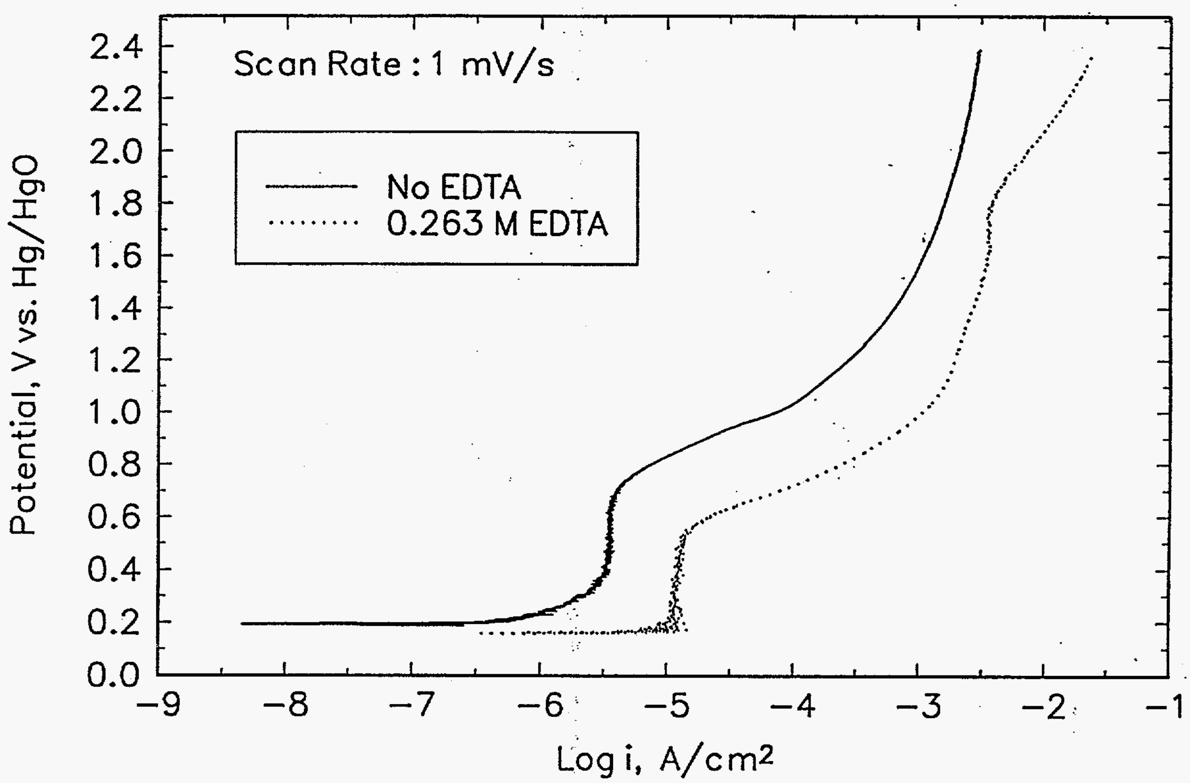

Figure 3. Potentiodynamic scans using platinum electrode, with and without Na_4EDTA, in NaOH solution (pH=12).

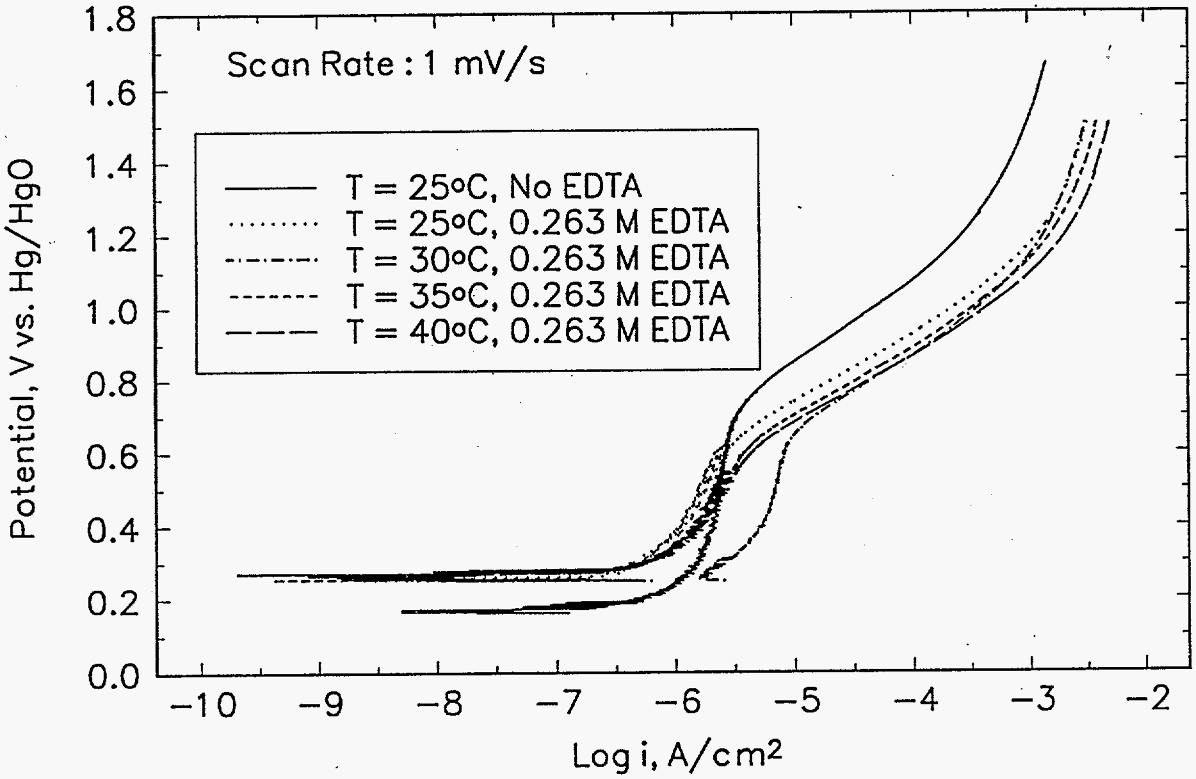

Figure 4. Potentiodynamic scans using platinum electrode in NaOH solution with 0.263 M Na_4EDTA (pH=12) at different temperatures.

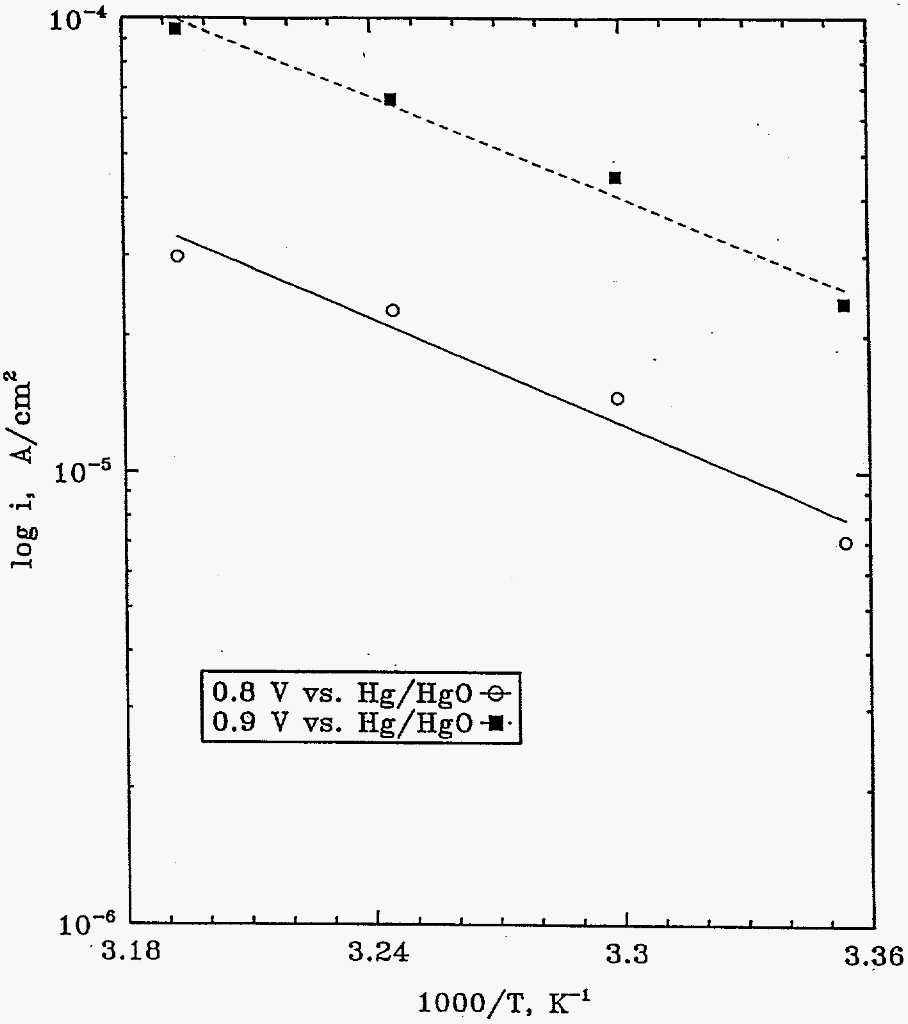

Figure 5. Effect of temperature on current density for the oxidation of 0.263 M Na_4EDTA using platinum electrode.

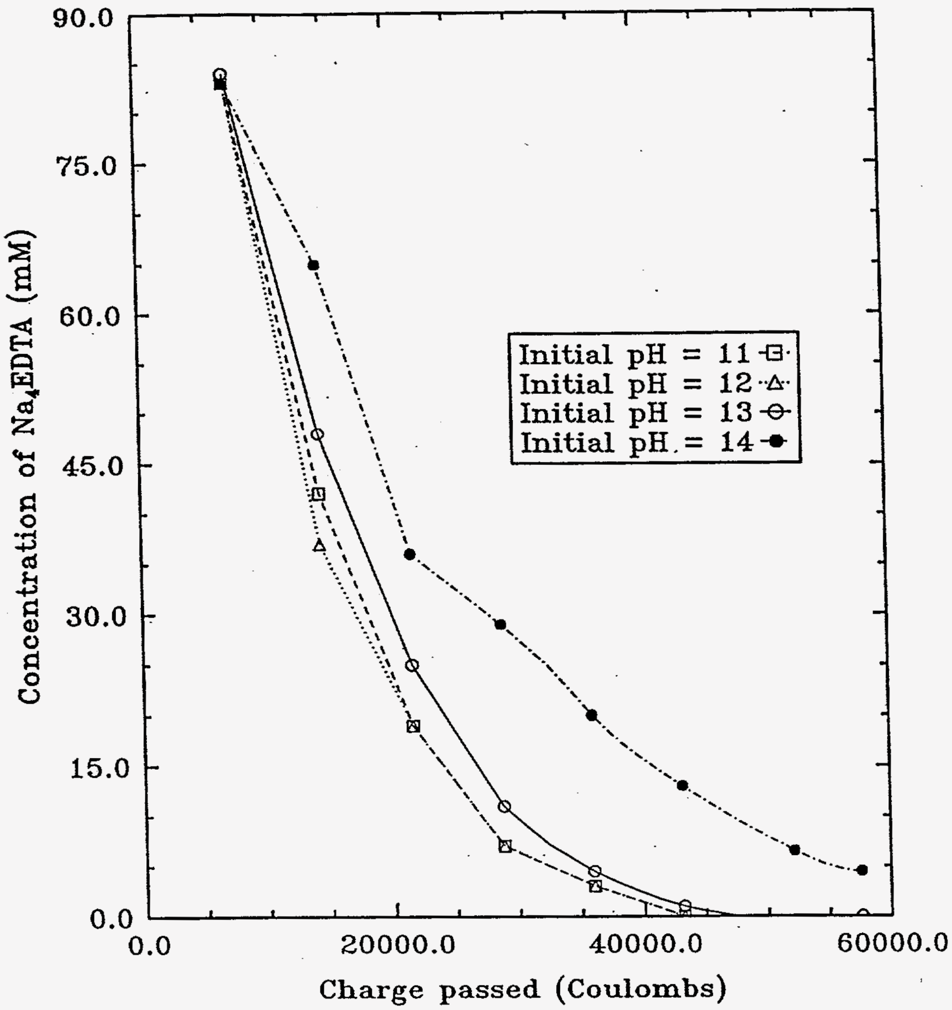

Figure 6. **Concentration of Na_4EDTA as a function of charge passed at different pH's.**