formation constants, K_f, for the copper(I) complexes with ethylene and carbon monoxide are evaluated as 7×10^5 and $2 \times 10^7\ M^{-1}$, respectively.

The estimated formation constant for the copper(I)–ethylene complex at 25 °C is greater by 14 times than that of the allyl alcohol.[15] This fact indicates that the oxygen atom does not take part in a bond formation in aqueous solution; in contrast, the oxygen coordinates to the copper atom in the solid state.[16] It is noteworthy that the compositions of these complexes are almost the same: $Cu(CH_2{=}CHCH_2OH)(H_2O)ClO_4$ and $Cu(CH_2{=}CH_2)(H_2O)_2ClO_4$.

Experimental Section

Measurements of Equilibrium Constants. The equilibrium constants of the complex formation with ethylene or carbon monoxide were determined at various temperatures. A mixture of copper powder and an aqueous solution of copper(II) perchlorate (0.02–0.05 M) was kept in vacuo in a constant-temperature bath. The ionic strength of the solution was adjusted to 1.0 by addition of sodium perchlorate. Ethylene and carbon monoxide were stored in the other side of the system and the pressure was measured with a mercury manometer by use of a cathetometer. The stopcock was opened to introduce the ethylene or carbon monoxide to the reaction vessel containing the copper(II) solution and copper. The reaction mixture was stirred for 1 or 2 days; then most of the gas phase was expanded into a space of known volume to measure the pressure. The gas phase was then expelled from the system for the purpose of diluting any possible impurities. The equilibrium pressure was measured 1 day later, at which time no pressure change had been observed.

Synthesis of the Ethylene Complex. Ethylene gas was passed through a reaction vessel containing copper(I) perchlorate hexahydrate (0.7 g), copper powder (1 g), and a stirring bar, until all of the air was replaced by ethylene. Methanol (2 ml) was then added by use of a microsyringe through a serum cup. The reaction mixture was stirred vigorously at room temperature while the ethylene flow was continued. The blue solution turned colorless within 1 h, indicating the completion of the reaction. The solution was filtered through a sintered-glass funnel by use of ethylene pressure. The solvent was removed by a stream of ethylene at room temperature. Colorless crystals, mp 30 °C, were obtained.

The complex was weighed in an atmosphere of ethylene and was connected to a gas buret. The ligand was freed by addition of a 0.1 N NaOH solution. The evolved gas was measured and identified as ethylene by use of ir. The precipitate was filtered and used for gravimetric analysis of copper as the cupferron complex. The filtrate was analyzed for perchlorate anion as nitron perchlorate.

Anal. Calcd for $Cu(C_2H_4)(H_2O)_2ClO_4$: Cu, 28.0; C_2H_4, 12.3; ClO_4, 43.8. Found: Cu, 27.9; C_2H_4, 12.2; ClO_4, 43.9.

Synthesis of the Allene Complex. In a vacuum system, allene was transferred to a reaction vessel containing a methanol solution of copper(II) perchlorate and copper powder. The mixture was stirred vigorously for 1 h. Excess copper was filtered off and the filtrate was evaporated in vacuo. The white powder remaining was analyzed as described above.

Anal. Calcd for $Cu_2(C_3H_4)(H_2O)_3(ClO_4)_2$: Cu, 30.0; C_3H_4, 9.53; ClO_4, 47.4. Found: Cu, 30.0; C_3H_4, 9.73; ClO_4, 47.3. The mole ratio of water to allene, as evaluated from the ^1H NMR spectra of the complex, was consistent with the calculated composition.

The Butadiene Complex. The copper(I) perchlorate complex of butadiene (mp 74 °C) was synthesized similarly to the allene complex.

Anal. Calcd for $Cu_2(C_4H_6)(H_2O)_4(ClO_4)_2$: Cu, 28.1; C_4H_6, 12.0; ClO_4, 44.0. Found: Cu, 28.0; C_4H_6, 11.9; ClO_4, 44.4. The ^1H NMR spectra showed that the mole ratio of water to butadiene was 4:1.

The Carbon Monoxide Complexes. The colorless crystalline complex (mp 10 °C) was synthesized similarly to the ethylene complex.

Anal. Calcd for $Cu(CO)(H_2O)_2ClO_4$: Cu, 28.0; CO, 12.3; ClO_4, 43.8. Found: Cu, 27.5; CO, 12.5; ClO_4, 43.6.

The white powdery complex was obtained by keeping $Cu(CO)(H_2O)_2ClO_4$ at 70 °C for 10 h under a nitrogen flow.

Anal. Calcd for $Cu_2(CO)_2(H_2O)_3(ClO_4)_2$: Cu, 29.2; CO, 12.9; ClO_4, 45.6. Found: Cu, 29.4; CO, 12.8; ClO_4, 45.9.

NMR Measurements. The samples for ^1H NMR measurements were prepared in the vacuum system. The NMR spectra were recorded with a 60-MHz spectrometer, Model JNM 3H60, of the Japan Electron Optics Laboratory, Ltd.

Ir Spectra. The ir spectra were obtained with a Hitachi EPI-G31. The spectrum taken in an NaCl cell was compared with that taken in a polyethylene film, since some of the complexes easily exchanged the anion. All of the samples were prepared in a nitrogen atmosphere.

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Registry No. $Cu(C_2H_4)(H_2O)_2ClO_4$, 59738-25-9; $Cu_2(C_3H_4)(H_2O)_3(ClO_4)_2$, 59811-73-3; $Cu_2(C_4H_6)(H_2O)_4(ClO_4)_2$, 59738-26-0; $Cu(CO)(H_2O)_2ClO_4$, 59729-20-3; $Cu_2(CO)_2(H_2O)_3(ClO_4)_2$, 59811-74-4.

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Equilibria of Ethylenediamine-*N*,*N*,*N*′,*N*′-tetrakis(methylenephosphonic) Acid with Cu(II), Ni(II), Co(II), Zn(II), Mg(II), Ca(II), and Fe(III) Ions in Aqueous Solution

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In a preliminary reinvestigation[1] of the complexing properties of ethylenediamine-*N*,*N*,*N*′,*N*′-tetrakis(methylenephosphonic) acid (EDTPO, H_8L), it has been shown that previous methods of preparation[2–6] were not entirely satisfactory and therefore the results reported in earlier work contain varying degrees of inaccuracy, depending on the purity of this interesting and important ligand. The analytically pure sample of EDTPO used in this investigation was obtained unambiguously through the quantitative mercuric chloride oxidation of the previously described well-characterized intermediate, ethylenediamine-*N*,*N*,*N*′,*N*′-tetrakis(methylene-

Table I. Proton Association Constants of EDTPO at 25.0 °C

Symbol	Equilibrium quotient	μ = 3.00 M		μ = 0.100 M	
		$\log K_n^H$	σ	$\log K_n^H$	σ
K_1^H	$\frac{[HL^{7-}]}{[H^+][L^{8-}]}$	12.01	0.0092	12.99	0.0049
K_2^H	$\frac{[H_2L^{6-}]}{[H^+][HL^{7-}]}$	9.02	0.0092	9.78	0.0073
K_3^H	$\frac{[H_3L^{5-}]}{[H^+][H_2L^{6-}]}$	7.42	0.0092	7.94	0.0073
K_4^H	$\frac{[H_4L^{4-}]}{[H^+][H_3L^{5-}]}$	5.88	0.0092	6.42	0.0073
K_5^H	$\frac{[H_5L^{3-}]}{[H^+][H_4L^{4-}]}$	4.77	0.0092	5.17	0.0073
K_6^H	$\frac{[H_6L^{2-}]}{[H^+][H_5L^{3-}]}$	2.82	0.0092	3.02	0.0073
K_7^H	$\frac{[H_7L^-]}{[H^+][H_6L^{2-}]}$	1.24	0.0092	1.33	0.0049

phosphonous) acid (EDTPI).[7]

Experimental Section

Preparation of Ethylenediamine-*N,N,N',N'*-tetrakis(methylenephosphonic) Acid (EDTPO). To 4.1 g (0.010 mol) of ethylenediamine-*N,N,N',N'*-tetrakis(methylenephosphonous) acid ($C_6H_{20}N_2O_8P_4 \cdot 2H_2O$) in 50 ml of hot water, 24 g (0.088 mol) of $HgCl_2$ in 100 ml of hot water was added and the mixture was boiled for 3 h. Mercury(I) chloride was removed and the filtrate was saturated with H_2S. The mercury(II) sulfide that formed was filtered off and the clear filtrate was evaporated to dryness, first under reduced pressure, then in a vacuum desiccator over $CaCl_2$ and KOH. The glassy residue crystallized upon treatment with a few milliliters of H_2O. Yield after methanol treatment was 4.7 g (100%). The product was recrystallized from hot water.

Anal. Calcd for $C_6H_{20}N_2O_{12}P_4 \cdot H_2O$: C, 15.87; H, 4.88; N, 6.17; P, 27.28. Found: C, 15.59; H, 4.84; N, 6.19; P, 27.71.

C, H, and N analyses were done at Kyushu University, Japan; P analysis was done by Chemalytics, Inc., Tempe, Ariz.

All metal salts used were of analytical grade from Mallinckrodt and their nitrate solutions were standardized by triple titrations with zinc metal standardized 0.0100 M EDTA solution.

Procedure. Accurately prepared 2.00×10^{-3} M solutions of EDTPO were measured potentiometrically in the absence and presence of equivalent and excess amounts of the metal ion as a function of added CO_2-free standardized 0.100 M KOH solution. The concentration of hydrogen ion, $[H^+]$, was monitored using established procedures described previously.[7] The pK_w values used in the calculations were 13.795 for the 0.100 M KNO_3 supporting electrolyte and 14.020 for the 3.00 M KNO_3 solution. The electrode system was calibrated by titration of standard HCl solution with standard KOH solution under the same conditions: KNO_3 electrolyte and 25.0 ± 0.05 °C. Absolute calibration was achieved by setting $\Delta pH = 0.000$ at p[H] of 1.997. This adjustment resulted in the direct correspondence of the pH meter readings with $-\log [H^+]$. When enough KOH solution had been added, the calculated p[H] was 11.752 at a dial reading of 11.746. Linear performance was assumed for pH meter reading between these two values.

Results

The concentration protonation constants at 25.0 °C determined at the two concentrations of the background electrolyte are listed in Table I. The values at 3.00 M KNO_3 have been calculated directly using an automated computer program for overlapping pK_a's. In the least-squares refinement, the quantity minimized is DH, the sum of the squares of the deviation ratios between calculated and observed hydrogen ion concentration over the entire potentiometric titration curve, where:

$$DH = \sum_{i=1}^{N} \{(([H^+]_{obsd})_i - ([H^+]_{calcd})_i)/([H^+]_{obsd})_i\}^2$$

The tabulated standard deviation, σ, refers to the calculated $-\log [H^+]$ curve compared with the measured curve involving the use of 47 equilibrium data points. The $\mu = 0.10$ values of the protonation constants are composites of the five inner values which calculated back the titration curve to within $\sigma = 0.0073$ as defined above and the two extreme values. Both the upper and the lower values listed were determined through the extrapolation from a least-squares plot of $\log K^H$ ($\mu = 0.100$) vs. $\log K^H$ ($\mu = 3.00$). The slope of 1.083 reflects the excess thermodynamic parameters which determine the activity coefficients in going from one medium to the other. The intercept of -0.0109 is near zero as charges on the ions approach zero. Extrapolation in this manner was resorted to because of the magnitude of the highest association constant, and therefore its value at $\mu = 0.100$ could not be measured directly. The standard error is 0.05 for this and the lowest pK_a's.

For each metal ion in Table II are listed the normal metal chelate formation constants K_{ML}, the four metal chelate protonation constants K_{MH_nL}, and the standard deviation, σ. In general, equilibrium data, such as shown in Figure 1 for each of the divalent metal ions studied, were at first assumed to represent the four chelate protonation equilibrium reactions (i.e., zero free metal). This is a very good approximation for Cu(II) but very poor for Mg(II) and Ca(II). Having obtained the initial values of K_{MHL}'s these were then used in the calculation of K_{ML} for each succeeding equilibrium point. Employing iterative techniques the equilibrium curves were calculated, $-(\log [H]_i)_{calcd}$, and compared with the experimental curves, $-(\log [H]_i)_{obsd}$. The σ, defined in this table,

Table II. Metal Chelate Formation Constants of EDTPO at 25.0 °C, μ = 0.100 M

Symbol	Equilibrium quotient	log *K*					
		Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Mg^{2+}	Ca^{2+}
K_{ML}	$\frac{[ML^{6-}]}{[M^{2+}][L^{8-}]}$	23.21	16.38	17.11	18.76	8.43	9.36
K_{MHL}	$\frac{[MHL^{5-}]}{[ML^{6-}][H^+]}$	7.56	8.94	8.31	8.31	9.95	9.42
K_{MH_2L}	$\frac{[MH_2L^{4-}]}{[MHL^{5-}][H^+]}$	5.99	7.40	6.49	6.06	8.79	8.44
K_{MH_3L}	$\frac{[MH_3L^{3-}]}{[MH_2L^{4-}][H^+]}$	4.62	5.48	5.29	4.99	6.96	6.59
K_{MH_4L}	$\frac{[MH_4L^{2-}]}{[MH_3L^{3-}][H^+]}$	3.74	4.33	4.30	3.10	4.97	5.25
	σ (for all above)[a]	0.0067	0.009	0.009	0.013	0.016	0.041

[a] $\sigma = \{\sum_{i=1}^{N}[(\log [H^+]_{obsd})_i - (\log [H^+]_{calcd})_i]^2/(N - 1)\}^{1/2}$ where $N \geq 56$ (number of data points).

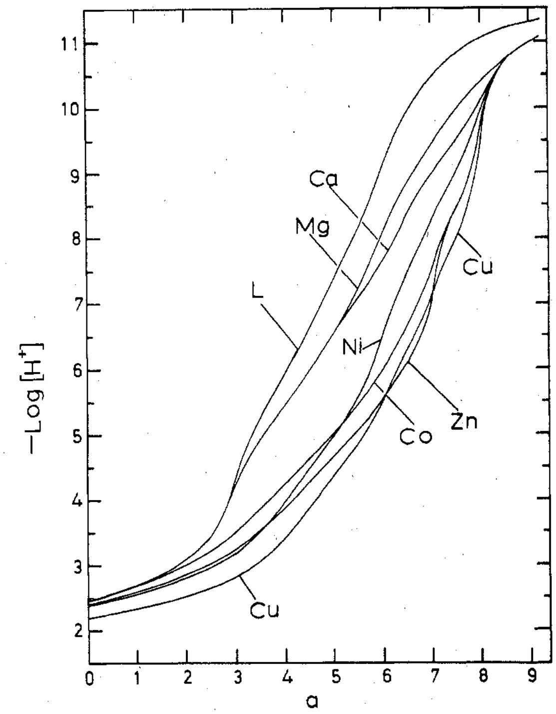


Figure 1. Potentiometric equilibrium curves for EDTPO with and without an equimolar mixture of Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Ca^{2+}, and Mg^{2+} measured at 25 °C, $\mu = 0.100$ (KNO_3), as a function of a (moles of KOH added/mole of ligand present). The initial concentration in all cases is 1.729×10^{-3} M. Each curve represents about 70 independent data points.

thus obtained was minimized through a refinement of the K_{MHL}'s based on the magnitude and the direction of the deviation of the calculated equilibrium curves from the observed curves in the specific regions which affect the particular K_{MH_nL}.

The presence of 2:1 (2M:1Lig) complex coordination was tested by using a 100% excess of Cu(II), Ni(II), Co(II), and Zn(II), and a 2000% excess of Mg(II) and Ca(II). Essentially the same K_{ML} was obtained in each case before precipitation of the excess metal took place. In the case of Ca(II) and Mg(II), no such precipitation occurred.

Discussion

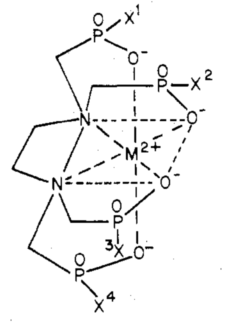
Protonation Constants. By now a definite pattern has emerged indicating the very high proton affinities of fully dissociated aminopolymethylphosphonic acids in moderate ionic solution such as 0.10 M KNO_3. The $-\log K^H$ values of nitrilotrimethylenephosphonic acid (NTPO), 12.34,[8] *N*-ethyliminodimethylenephosphonic acid, 12.42,[8] ethylenediamine-*N*,*N*-bis(1,1-dimethylmethylenephosphonic) acid, 11.68,[9] and ethylenediaminedimethylenephosphonic acid, 10.60[7] and 10.47,[9] are high, but not as high as 12.99 for EDTPO. This latter figure is indicative of the cumulative electrostatic effects of the octanegative EDTPO anion taken with the various favorable ways in which a given proton could "chelate" within this negative cavity.

The nature of the successive protonation steps may be assigned on the basis of the electrostatic considerations and the values of the log protonation constants (log K_n^H's) of analogous compounds such as ethylenediamine[10] (10.04, 9.89), methylphosphonic acid[11] (7.9, 2.3), and ethylenediamine-*N*,*N'*-dimethylenephosphonic acid.[7] Thus the first protonation takes place on one of the internal nitrogen atoms. HL^{7-} can be protonated in only one way, on the remaining nitrogen. The third proton in H_3L^{5-} may coordinate to any of the 12 equivalent oxygen positions, and so on. However, any of the more highly protonated ligands should be considered as thermodynamic entities each composed of several microspecies in equilibrium.

In comparing the available literature values of the protonation constants of EDTPO with the present results, the earliest reference[2] shows the largest disparity. This is understandable in view of the reported physical properties of the ligand. The relatively recent work of Tikhonova[12] (10.68, 9.21, 7.66, 6.59, 5.64, 3.74, 2.72, 1.50) differes from that of Kabachnik et al.[4] (12.10, 10.18, 8.08, 6.54, 5.23, 3.0) which in turn differs from ours (12.99, 9.78, 7.94, 6.42, 5.17, 3.02, 1.33). Uhlig[5] appears to have come the closest yet every reference cited failed to determine correctly the first protonation constant, which is at least one order of magnitude higher than had been reported.

Metal Chelate–Proton Equilibria. The value of log K_{ML} for Cu(II) with EDTPO is the highest ever reported for copper and indicates the exceptionally high affinity of the ethylenediaminetetramethylenephosphonate ligand, L^{8-}, for Cu(II). The log normal stability constant for EDTA[10] with Cu(II) is only 18.70, some 4.5 orders of magnitude less than EDTPO. The only other exceptional K_{ML} value is found for zinc, which is about two orders of magnitude higher than with EDTA (16.44).[10] All the others are inexplicably lower: log K_{ML} (Ni) is 18.52 (EDTA),[10] Co(II) is 16.26 (EDTA),[10] and so on. This unique reversal of the usual stability order is interesting and suggests further equilibrium studies with highly negatively charged multidentate ligands.

The fact that the ligand forms only mononuclear complexes with the potentiometric data calculable to such high precision using only four protonated species simplifies the problem of assignment of the structure of the various MH_nL species in solution. All the data, including the fundamental properties of metal ions, as well as the stepwise decrease in the magnitude of the chelate protonation constants, are consistent with the arrangement of ligand donor groups indicated by I.



MH_nL, $n = 0, 1, 2, 3, 4$; X = OH or O^-

I

For a moderately strongly coordinating metal ion, as the pH is raised the initial coordination reaction forms MH_4L^{2-} followed by successive deprotonation to MH_3L^{3-}, MH_2L^{4-}, MHL^{5-}, and ML^{6-}.

The fact that the 2 to 1 experiments yielded the same values for the calculated constants provided indirect evidence that the metal ion is coordinated through both nitrogen atoms of the ligand. Thus if only one amino group were involved, evidence for 2:1 (2M:L) complexes would have appeared. Under the special conditions of extremely high concentrations other species may take on some importance, but in dilute solutions the sequence outlined above seems to hold. Potentiometric equilibrium measurements of a 1:1 molar ratio of Fe(III) and EDTPO were carried out, but the protonated chelate compound formed was found to be insoluble. At seven equivalents of KOH the iron(III) chelate dissolved and an equilibrium determination of the protonation constant of the iron(III) chelate was determined ($K_{MHL} = 10^{6.5}$). For the analogous thorium(IV) complex, a white precipitate, formed at pH ~2, persisted through pH ~6, at which point it dissolved. However, the pH of the system kept drifting, presumably because of a slow hydrolytic reaction of the thorium(IV) chelate, and no equilibrium calculations could be carried out.

Aminophosphonic acids are becoming increasingly important for biological systems as well as in the design of new synthetic ligands as sequestering agents for metal ions.[13] This note provides new evidence for the effectiveness of aminophosphonate donor groups in the binding of metal ions, and provides more precise data for the phosphonate analogue of EDTA.

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Registry No. CuH_4L, 59710-55-3; NiH_4L, 59710-56-4; CoH_4L, 59710-57-5; ZnH_4L, 59710-58-6; MgH_4L, 59710-59-7; CaH_4L, 59710-60-0; FeH_4L, 59710-61-1.

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Kinetics and Mechanism of μ-Oxo Dimer Formation by Ethylenediaminetetraacetatatoiron(III), [FeEDTA]⁻

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The reactions of the FeEDTA system have attracted considerable attention for their importance in inorganic chemistry,[2-4] in biochemistry,[4-6] as catalysts,[7-9] and in industrial chemistry.[10] Martell and Gustafson[2] carried out early investigations of the thermodynamics of the interaction of Fe^{3+} and $EDTA^{4-}$ and identified several major species, including $[FeEDTA]^-$, its hydrolyzed form $[FeEDTAOH]^{2-}$, and a hydrolyzed dimer, and defined the equilibria between these species. The later investigations of Schugar and Gray,[3a,4] Walling,[9] and others coupled with the crystallographic determination of the structure of the analogous FeHEDTA dimer[11] showed the binuclear species to be an oxo bridged complex $[(FeL)_2O]^{(2n-4)-}$ (H_nL = EDTA, HEDTA (*N*-hydroxyethylethylenediaminetriacetic acid, NTA (nitrilotriacetic acid), . . .), characterized by strong exchange interaction of the iron centers through the nearly linear oxo bridge. (Such linearity is consistent with maximum spin pairing.[12])

This extensive delocalization through an oxo bridge is reflected in the strongly reduced magnetic susceptibility of the dimer (and its antiferromagnetic behavior), as well as in the spectral properties of the dimer, which exhibits a characteristic Fe–O–Fe stretch at approximately 840 cm^{-1}, and a series of uv–visible bands of enhanced intensity,[4] with molar absorptivities (for $[(FeEDTA)_2O]^{4-}$ $\epsilon_{475} = 180\ M^{-1}\ cm^{-1}$) two orders of magnitude larger than the corresponding mononuclear complexes, resulting in the dark red-orange color of solutions in which dimer is present. Gray has reviewed the spectral and magnetic properties of oxo bridged iron complexes, with special emphasis on the biochemical significance of such complexation.[4]

Thus, the identity of the major species in solution and the thermodynamics governing their interconversions have been established. The pathway for this interconversion, however, has remained unclear. In the present work, we have determined the kinetics of dimer formation and decomposition, and thereby established the probable pathway for the dimerization reaction.

Materials and Methods

Ferric solutions were prepared by dissolving reagent grade $Fe(NO_3)_3$ in acidic distilled water, and standardized by EDTA titration. All spectra were obtained on a Cary 14 spectrophotometer using matched 1.00 cm cells. For the determination of the dimerization constant under present experimental conditions, absorbance at 475 nm was monitored as a function of pH and metal ion concentration. With the value of $\epsilon_{dimer} = 180\ M^{-1}\ cm^{-1}$ and the application of the appropriate hydrolysis and formation constants,[2] together with the appropriate mass balance equations, a value of K_{dimer} was obtained. It should be noted that this value is quite sensitive to the extinction coefficient, so that the errors inherent in the method are rather high. The method of limiting spectra cannot be used, since dimer never reaches >70% of the possible total.

Kinetic runs were monitored on a Durrum Gibson D150 stopped flow spectrophotometer by following dimer concentration at 475 nm. For the dimerization reaction, a low pH solution of $[FeEDTA]^-$ was mixed with a high pH buffer solution (ammonia and borate were both used with essentially identical results). Dimerization data were analyzed by calculating the concentration of dimer at time *t*, using $\epsilon_{dimer} = 180\ M^{-1}\ cm^{-1}$, and the known path length of the flow cell. Concentration of the mononuclear species was then obtained from the mass balance equations. Analogously, in the monomerization reaction, a high pH solution of FeEDTA, in which dimer formation was maximal, was reacted with a low pH buffer solution (potassium acid phthalate or phosphate, pH 5.5–7.0).

Results and Discussion

Spectra of the $Fe^{III}EDTA$ system as a function of pH are given in Figure 1. The band at 475 nm, which is characteristic of dimer formation,[4] increases with increasing pH, as required by eq 1. As the p*K* for hydrolysis of the $[FeEDTA]^-$ species

$$2[\mathrm{FeEDTA}]^- \rightleftharpoons [(\mathrm{FeEDTA})_2\mathrm{O}]^{4-} + 2\mathrm{H}^+ \qquad (1)$$

to $[FeEDTAOH]^{2-}$ is approximately 7.4, above pH 9.4 essentially all monomeric FeEDTA will be converted to the hydrolyzed forms. The dimerization reaction of $[FeEDTAOH]^{2-}$ is pH independent as shown in eq 3 and dependent only on concentration.

$$[\mathrm{FeEDTA}]^- \overset{K_{OH}}{\rightleftharpoons} [\mathrm{FeEDTAOH}]^{2-} + [\mathrm{H}^+] \qquad (2)$$

$$2[\mathrm{FeEDTAOH}]^{2-} \overset{K_d}{\rightleftharpoons} [(\mathrm{FeEDTA})_2\mathrm{O}]^{4-} \qquad (3)$$

The study of the 475-nm peak as a measure of dimer formation yields a dimerization constant which depends only on temperature and ionic strength. At 25.0 °C and $\mu = 1.00$ M, log $K_d = 2.8 \pm 0.2$[2] and at $\mu \cong 0.50$ M (the ionic strength de-