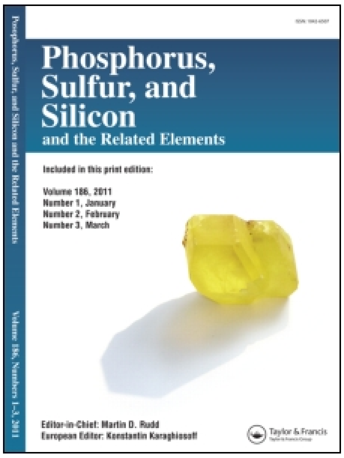

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# Speciation Studies of Iron (III) with (Poly)phosphonate Ligands: The Case of EDTMP (EthylenediamineTetramethylene Phosphonic Acid)

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# Speciation Studies of Iron (III) with (Poly)phosphonate Ligands: The Case of EDTMP (Ethylenediamine-Tetramethylene Phosphonic Acid)

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*The complex formation equilibrium of ethylenediaminetetramethylenephosphonic acid (EDTMP, $H_8L$) with iron (III) has been studied potentiometrically at 25°C and an ionic strength of 0.2 M (NaCl). The successive protonation constants of ligand EDTMP and the complex formation constants were determined with the PSEQUAD program. Keeping in view the biological studies, the speciation in the system Fe (III)—EDTMP was calculated and drawn with the HySS computer program, and pFe values are compared.*

**Keywords** EDTMP; Fe (III); HySS; potentiometry; PSEQUAD; speciation

## INTRODUCTION

Magnetic Resonance Imaging (MRI) has become one of the primary imaging modalities in modern medicine. With the widespread use of MRI, there is an increasing demand for efficient paramagnetic contrast agents used to enhance the differences between normal and diseased tissue or to indicate specific organ functions. Complexes of some paramagnetic transition metal and rare earth ions have been considered as potential contrast agents.[1,2] The complexes mentioned

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in the literature[3–10] are polyaminopolycarboxylate coordination compounds.

Polyaminopolycarboxylates (PAPC), represented first of all by ethylenediamine-N,N,N′,N′-tetraacetate (EDTA), have been extensively characterized with respect to analytical and coordination chemistry. The polyaminopolyphosphonates (PAPP) were synthesized for the first time by Schwarzenbach and colleagues[11] and have been used for industrial purposes such as a scale inhibitor for oil drilling and geothermal power plants. However, their properties are not so well understood as compared to those of PAPC.

These PAPP have high first-protonation constants relative to those of corresponding PAPC. In the case of ethylenediamine-N,N,N′N′-tetramethylenephosphonate ($EDTMP^{8-}$) thermodynamic[12] and $^{31}P$ NMR studies[12,13] revealed that protonation equilibria are rather complicated. On the other hand, the first protonation occurs on the nitrogen atom and forms a hydrogen bond between both nitrogen atoms ($NH^+ \cdots N$). The second protonation predominantly occurs on the phosphonate oxygen atom because of the decrease in the basicity of an unprotonated nitrogen atom due to the formation of a hydrogen bond, and both of the nitrogen atoms are protonated at the third protonation.

This work is part of a wider project seeking to compare and/or correlate the physical parameters of different metal-ligand equilibria, determined with recent computer programs, and hence, under identical conditions. This article presents the results of some aqueous solution studies concerning the formation, stability, and speciation of the coordination compounds of Fe (III) with EDTMP.

## EXPERIMENTAL

Potentiometric titrations were performed with a CG 841 Schott pH-meter equipped with a glass electrode N 6280. The pH electrode was calibrated using two standard buffer solutions. All calibrations and titrations were carried out in a glass vessel (25 $cm^3$) under a $CO_2$-free nitrogen atmosphere to avoid any contact with carbon dioxide. The temperature was regulated at $25.0 \pm 0.1^\circ C$, and an ionic strength of 0.2 M NaCl was maintained. As a titrant, a $CO_2$-free solution was used, which consisted of 0.078 M KOH and 0.120 M NaCl, to minimize the ionic strength change during titration.

The potentiometric equilibrium studies were made with ligand solutions at different concentrations: in the absence of ferric ions, and then in the presence of metal ions with the M:L ratios 1:1, 1:2, and 1:4, respectively. The pH data were obtained after the addition of 0.100 $cm^3$ increments of a standardized KOH solution.

At low values of a pH, a solid phase appears in the solution in the presence of ferric ions. This phase disappeared at pH 2.50 in a solution with an M:L ratio of 1:4, at pH 4.76 in a solution with an M:L ratio of 1:2, and at pH 5.79 in a solution with an M:L ratio of 1:1. For the calculation of overall stability constants, only the pH values for clear solutions were considered. At pH values between 5 to 8, the equilibrium was attained slowly, and about 5 min was required for each point of the titration.

A stock solution of 0.01784 M $Fe^{3+}$ in $2.10^{-2}$ M HCl was prepared from $FeCl_3$ and a standardized HCl solution. The titrant solution was prepared from KOH and it was standardized with potassium hydrogeniodate.

The ligand was synthesized in the laboratory,[14] and the purity of ligand was confirmed by titration with a standardized $ZnSO_4$ solution in the presence of Eriochrom black T at a buffered value of pH = 10.

The protonation constants of the ligand and the overall stability constants of the various ferric complexes formed in an aqueous solution were determined from the titration data with the Fortran computer program PSEQUAD.[15] Species distribution diagrams were computed from the overall formation constants with HySS computer program.[16]

The $pK_w$ value for the aqueous system, defined as $-\log [H^+] \cdot [OH^-]$ at the ionic strength employed, was 13.74 at 25°C.[17]

## RESULTS AND DISCUSSIONS

The reactant concentrations used in these studies, along with the pH ranges on which the calculations are based, are reported in Table I. The measurements made at acidic pH, where the solid complexes of Fe (III) were separated, were not included in the final calculations.

The titration curves of the ligand, in the absence or in presence of different concentrations of ferric ions, indicate the formation of ferric chelates containing hydrogen ions in addition to the metal. At a higher

**TABLE I Summary of the Titration Data Used for Calculating Formation Constants**

| System | $C_{Fe}$ ($mmol \cdot dm^{-3}$) | $C_L$ ($mmol \cdot dm^{-3}$) | $C_H$ ($mmol \cdot dm^{-3}$) | pH range used for the calculation | $n^a$ |
|---|---|---|---|---|---|
| proton—edtmp | | 1.936 | | 2.125–11.317 | 61 |
| (25°C) | | 0.968 | | 2.515–11.120 | 32 |
| | 1.784 | 1.936 | 2.000 | 5.787–11.161 | 23 |
| Fe (III)—edtmp | 0.856 | 1.936 | 0.960 | 4.763–11.327 | 35 |
| (25°C) | 0.428 | 1.936 | 0.480 | 2.505–11.404 | 54 |

[a] n represents the number of experimental observations in each titration.

pH, all the acidic chelates go over to the "normal" chelates from which all the dissociable hydrogens have been displaced.

The protonation constants of EDTMP were calculated by fitting the potentiometric data obtained for the free ligand to the PSEQUAD program[15]. The initial computations were obtained in the form of overall protonation constants $\beta_i = [\mathrm{H_iL}]\cdot[\mathrm{L}]^{-1}\cdot[\mathrm{H}]^{-\mathrm{i}}$. Table II gives the protonation constants of EDTMP—our data and literature values—calculated as $\mathrm{K_i^H} = \frac{[\mathrm{H_iL}]}{[\mathrm{H_{i-1}L}]\cdot[\mathrm{H}]}$, taking into account that $\beta_\mathrm{i} = \prod_{\mathrm{i=1}}^{\mathrm{i=6}} \mathrm{K_i^H}$.

As pointed out by Motekaitis and colleagues,[22] the values reported before 1976 may contain a considerable degree of inaccuracy because of an impure reagent or an imperfect analysis of data. As an example, until 1976 the protonation constants of EDTMP were generally calculated by Schwarzenbach's and Ackermann's[26] graphical method with a small modification based on the assumption that the number of protonated species dominant within a buffer region is restricted. After 1976 an efficient computer program was developed for these calculations. Details about the protonation of EDTMP can be found in the literature.[12,24,27]

The stability constants of the various species formed in the aqueous solution were obtained from the experimental data of titrations of a solution with a different ligand: ferric ions ratios, using the same program. As for the ligand, the initial computation was obtained in the form of the overall stability constants $\beta_\mathrm{mlh} = [\mathrm{M_mL_lH_h}]\cdot[\mathrm{M}]^{-\mathrm{m}}\cdot[\mathrm{L}]^{-\mathrm{l}}\cdot[\mathrm{H}]^{-\mathrm{h}}$, in

**TABLE II Protonation Constants of the Ligand (EDTMP) (25°C, I = 0.2 M NaCl) Compared With the Literature Data**

| | | Literature data | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\mathrm{pK_i}$ | This work[a] | 18[b] | 19[b] | 20[c] | 21[c] | 22[b] | 23[b] | 24[b] | 25[d] |
| $\mathrm{pK_1}$ | 11.33 (2) | 10.21 | 10.60 | 12.10 | 10.68 | 12.99 | 10.60 | 13.0 | 9.64 |
| $\mathrm{pK_2}$ | 9.14 (4) | 9.91 | 9.22 | 10.18 | 9.21 | 9.78 | 10.48 | 9.85 | 7.69 |
| $\mathrm{pK_3}$ | 7.44 (5) | 8.02 | 7.43 | 8.08 | 7.66 | 7.94 | 9.27 | 7.87 | 6.27 |
| $\mathrm{pK_4}$ | 6.06 (5) | 7.14 | 6.63 | 6.54 | 6.95 | 6.42 | 7.39 | 6.40 | 5.04 |
| $\mathrm{pK_5}$ | 4.85 (6) | 5.25 | 6.18 | 5.23 | 5.64 | 5.17 | 5.63 | 5.12 | 2.86 |
| $\mathrm{pK_6}$ | 1.66 (22) | 4.41 | 5.05 | 3.00 | 3.72 | 3.02 | 3.80 | 2.96 | 1.12 |
| $\mathrm{pK_7}$ | — | 2.77 | 2.72 | — | 1.50 | 1.33 | 2.73 | <1 | <1 |
| $\mathrm{pK_8}$ | — | 2.45 | 1.46 | — | — | — | 2.43 | <1 | < 1 |

[a] Fitting (average difference between experimental and calculated titration curves expressed in $\mathrm{cm^3}$ of titrant) 0.0148; number of points 93; values in parenthesis are standard deviations in the last significant digit.

[b] 25°C, $I = 0.1$ M ($\mathrm{KNO_3}$).

[c] 25°C, $I = 0.1$ M (KCl).

[d] 25°C, $I = 0.15$ M (NaCl).

which the subscript *m* stands for metal, *l* for ligand, and *h* for proton. For these calculations, the fact that ferric ions form several hydrolytic species in an aqueous solution was taken into account. There is a disagreement on the subject of their values in the literature. We have used the values reported by Achour and colleagues,[28] which are considered reliable. The hydrolysis constants of the $Fe^{3+}$ ions used in this work are

$$\log\beta_{[FeOH]/([Fe][OH])} = 11.29, \quad \log\beta_{[Fe(OH)_2]/([Fe][OH]^2)} = 21.74, \quad \log\beta_{[Fe_2(OH)_2]/([Fe]^2[OH]^2)} = 24.84. \tag{1}$$

To examine the experimental data, the protonation curves of the ligand in the presence of iron (III) were compared with the reference curves obtained in its absence (Figure 1). All these curves represent variations of the average ligand protonation number ($\bar{r}$) as a function of pH:

$$\bar{r} = \frac{C_H + 8 \cdot C_L - C_{OH} + [OH] - [H]}{C_L} \tag{2}$$

where $C_H$, $C_L$, and $C_{OH}$ are the total concentrations of protons (added with a stock solution of iron), ligand, and KOH titrated, respectively.

For the ligand EDTMP at high pH, the curve levels off at about 1 indicating that the last proton cannot be removed. Below pH = 3, the curve levels off at about 6, and this indicates that 6 protons have been

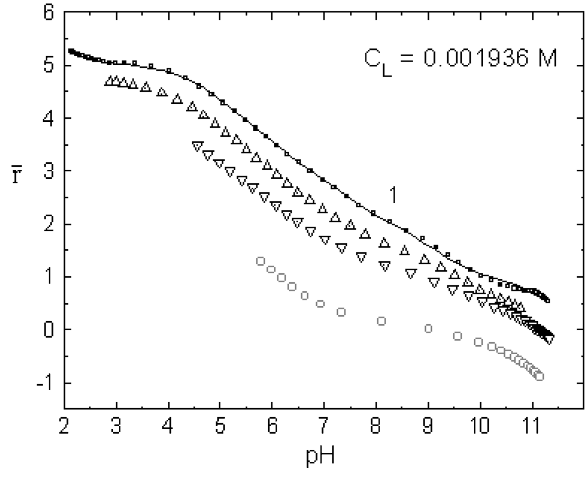

**FIGURE 1** Protonation curves for (1) ligand (solid line represent calculated function), (circle) ligand: Fe (III) = 1:1, (down triangle) ligand: Fe (III) = 2:1, (up triangle) ligand: Fe (III) = 4:1; all curves were calculated from potentiometric data obtained at 25°C and I = 0.2 M (NaCl).

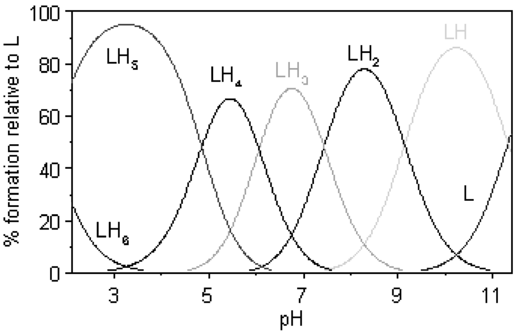

**FIGURE 2** Speciation diagrams of the ligand, calculated for $C_L = 0.001936$ M, at 25°C and $I = 0,2$ M (NaCl).

added to the ligand. These 6 protonation constants have been determined in this study. The agreement between the calculated function and experimental data is good, which confirms the chosen model. The plateau at $\bar{r} = 5$ and a pH between 3 to 4 indicates that the species with 5 protons is the dominating species. The speciation diagrams of the ligand, in Figure 2, calculated with HYSS[16] confirm that $LH_5^{3-}$ dominates between pH values 3 to 4. Potentiometric, protonation, and speciation curves indicate that not all the phosphonate groups are deprotonated until pH values around 10 to 11 are reached.

Westerback and colleagues[19] reported the formation and protonation constants of EDTMP complexes with ferric ions, and their values agree with our data, as shown in Table III. It is seen here that the logarithms

**TABLE III Overall Formation Constants of Fe (III)—EDTMP Complexes: Comparison with Literature Values**

| | | log $\beta_{mlh}$ | |
|---|---|---|---|
| Complex | Species *mlh* | This work[a] | 19[b] |
| FeL(OH) | 1 1 −1 | 8.39 (9) | — |
| FeL | 1 1 0 | 20.07 (5) | 19.60 |
| FeLH | 1 1 1 | 26.56 (6) | 26.74 |
| $FeLH_2$ | 1 1 2 | 31.65 (6) | 33.02 |
| $FeLH_3$ | 1 1 3 | 36.12 (7) | — |

[a] Fitting 0.0233; number of points 114; values in parenthesis are standard deviations in the last significant digit.

[b] 25°C, $I = 0.1$ M ($KNO_3$).

**TABLE IV Formation Constants of Fe (III)—EDTMP Complexes (log $K_{mlh}$): Comparison With Literature Values of Fe (III)—EDTA Complexes**

| | | Fe (III)—EDTA complexes (log $K_{mlh}$) | | | |
|---|---|---|---|---|---|
| Equilibrium quotient | This work | 29 (I = 0) | 30 (I = 0.1 M) | 31 (I = 1 M) | 32 (I = 0.1 M) |
| [FeL]/[Fe][L] | 20.07 | 24.23 | 23.75 | | 25.1 |
| [FeLH]/[Fe][HL] | 15.23 | 15.26 | 14.59 | 15.2 | |
| $[FeLH_2]/[Fe][H_2L]$ | 11.18 | 8.72 | | | |
| $[FeLH_3]/[Fe][H_3L]$ | 8.54 | | | | |
| [FeL(OH)]/[FeL][OH] | 2.06 | | | 7.1 | 6.5 |

of the normal chelate stability constant ($\beta_{110}$) for the combination of the $Fe^{3+}$ with an octanegative EDTMP anion ($L^{-8}$) are calculated as 20.07 at 25°C. Because the stability is sufficiently high, it can be inferred that a solution of iron (III) chelate may be stored at a pH of about 11 for a number of weeks without developing any sign of the precipitation of ferric hydroxide.

As can be observed from Table IV, the formation constant of the normal chelate of Fe (III) with EDTMP (log $K_{110} = 20.07$) is much smaller than that of the EDTA chelate (log $K_{110}$ = 23.75–25.10). This indicates that one of the nitrogen atoms of EDTMP is not engaged in coordination[33]. As log $K_{110} = 20.07 >$ log $K_{111} = 15.23$, this suggests a very strong Fe—N bond, which, in a protonation complex, cannot be ruptured.[34] Consequently, the protonation of the FeL chelate occurs on the free oxygen atoms of the phosphonate groups of the complex.

The speciation diagrams (Figure 3) show that the FeL species exist in a great percentage in the pH range of 7–11. Therefore, in the basic range, most of the monoprotonated complexes undergo deprotonation:

$$FeLH^{4-} \rightleftharpoons FeL^{5-} + H^+ \quad K_1 = \frac{[FeL]\cdot[H]}{[FeLH]} = 10^{-6.49} \tag{3}$$

Analogically, the deprotonation of the two protonated Fe (III)—EDTMP chelates ($FeLH_2$ and $FeLH_3$) can be written and calculated as follows:

$$K_2 = \frac{[FeLH]\cdot[H]}{[FeLH_2]} = 10^{-5.09} \quad \text{and } K_3 = \frac{[FeLH_2]\cdot[H]}{[FeLH_3]} = 10^{-4.47} \tag{4}$$

The fact that the first protonation constant of the complex (log $K_{1p}$ = 6.49) is smaller than the second protonation constant of the ligand (log $K_2 = 9.14$) indicates that the first protonation occurs on the free oxygen atoms of the phosphonate groups of the complex.[35] Similarly, the second

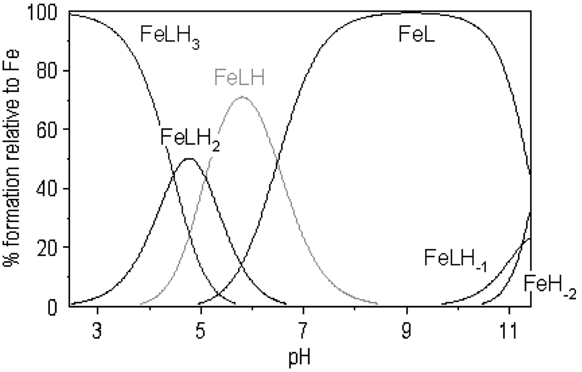

**FIGURE 3** Speciation diagrams of the Fe (III)—EDTMP chelates, calculated for $C_L = 0.001936$ M, $C_{Fe} = 0.000428$ M, at 25°C and I = 0.2 M (NaCl).

protonation constant of the complex ($\log K_{2p} = 5.09$) is smaller than the third protonation constant of the ligand ($\log K_3 = 7.44$). For the third protonation process, $\log K_{3p} = 4.47$ is smaller than the fourth protonation constant of the ligand ($\log K_4 = 6.06$). From this it can be surmized that the second and third protonation of the Fe (III)—EDTMP complexes also occur on the free oxygen atoms of the phosphonate groups of the complex.

The evaluation of the behavior of the ferric ion complexes of EDTMP for medical application cannot be made by stability constant values. In a blood stream, other species such as $Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, and $H^+$ are present and may compete with the ferric ions for the formation of the metal complex with other ligands, such as transferrin.[28] To avoid the transfer of the ferric ion to the biomolecule, which can be fatal if toxic or radioactive ions are used, the complex formed with EDTMP needs to be particularly stable and highly selective. pFe values (pFe = $-\log [Fe^{3+}{}_{free}]$), given in Table V, are a more reliable choice for the evaluation of ligand effectiveness, especially when taking into account the protonation constants of the ligand at physiological pH (pH = 7.40) when the total ligand concentration is twice that of the total iron concentration.

Due to the dependence of pFe on the ligand protonation constants, very different predictions about in vivo stability can result if $\log K_i$ or pFe values are compared. The larger the pM values (calculated for 100% excess of a free ligand at physiological conditions, pH = 7.4, $C_{Fe} = 1 \cdot 10^{-5}$ M, $C_L = 2 \cdot 10^{-5}$ M) the more effective is the ligand. The relative order of the pFe values may change if a different set of conditions is used to calculate the pFe values. Moreover, for biological studies, the conditional stability constant of a metal chelate under

**TABLE V pFe and Conditional Stability Constant (log $K'_{FeL}$) at 25°C and I = 0.2 M (NaCl)**

| $C_L$ (mM) | $C_{Fe}$ (mM) | pFe[a] | log $K'_{FeL}$ |
|---|---|---|---|
| 1.928 | 1.784 | 13.04 | |
| 1.928 | 0.856 | 14.19 | |
| 1.928 | 0.428 | 14.69 | 14.12 |
| 0.002 | 0.001 | 13.54 | |
| 0.050 | 0.001 | 15.83 | |

[a] pFe values were calculated at physiological pH (7.4).

physiological conditions (pH = 7.4) is more important than the overall stability constant.[36]

Figure 3 shows that at physiological pH, about 85% of ferric ion complexes of EDTMP, exist as normal FeL chelate and about 15% exist as a monoprotonated FeLH chelate. Table V contains the pFe values calculated for different conditions as well as the conditional stability constants of a the normal chelate. The computer program PSEQUAD[15] can calculate the concentration of a free aqua ferric ion [$Fe^{3+}_{free}$] at any experimental point. In the titration data, the existence of the value of 7.4 for the pH is essential. However, the titration curves of mixtures Fe:L in the pH domain of 6–9 show no plateau, so the value 7.40 for the pH is almost impossible to attain. This is the primary reason for which the HySS computer program was used.[16]

In case side reactions occur in a solution, the value of the constant $K_{ML}$ is substituted by a conditional stability constant $K'_{ML}$ defined as[37] follows:

$$K'_{ML} = K_{ML} \cdot \frac{\alpha_{ML}}{\alpha_M \cdot \alpha_L} \tag{5}$$

where $\alpha_M, \alpha_L$, and $\alpha_{ML}$ represent the side reaction coefficient of the metal ion, the ligand, and the formed complex. The pH value influences $\alpha_M, \alpha_L$, and $\alpha_{ML}$, and the presence of other metal ions influences $\alpha_L$. For the FeL chelate, a side reaction coefficient of normal chelate, $\alpha_{ML}$, can be calculated as follows:

$$\alpha_{FeL} = 1 + \frac{\sum_{h} \beta_{11h} \cdot [H^+]^h}{\beta_{110}} \quad \text{where} \quad h = -1, 1, 2, \text{and } 3 \tag{6}$$

The side reaction coefficient for EDTMP is as follows:

$$\alpha_L = 1 + \sum_{i=1}^{i=6} \beta_i \cdot [H^+]^i \tag{7}$$

**TABLE VI log $K_{ML}$ and pM Values for $Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, and $Fe^{3+}$ Complexes of EDTMP at 25° $C_L = 0.002$ mM, $C_M = 0.001$ mM, and I = 0.2 M (NaCl)**

| Cation | log $K_{ML}$ | pM[b] |
|---|---|---|
| $Ca^{2+}$ | 9.29[a] | 8.05 |
| $Mg^{2+}$ | 8.43[a] | 8.57 |
| $Zn^{2+}$ | 18.76[a] | 12.76 |
| $Fe^{3+}$ | 20.07 | 13.54 |

[a] Values from.[22]

[b] pM values were calculated at physiological pH (7.4).

Because at pH < 10 the concentration of hydrolytic species of ferric ions is extremely reduced, the formation of these species can be neglected (*cf.* Figure 3), and consequently, for ferric ions, $\alpha_M = 1$.

In Table VI, pM values for $Ca^{2+}$, $Mg^{2+}$, and $Zn^{2+}$ were calculated with the HySS program at 25°C, $C_L = 0.002$ mM, $C_M = 0.001$ mM, and I = 0.2 M (NaCl) on the basis of the formation constant calculated by Motekaitis and colleagues.[22] These results indicate that the competition among $Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, and $Fe^{3+}$ with EDTMP is seen to favor $Fe^{3+}$ at pH = 7.4. Therefore, the iron (III) complex should be stable enough to avoid interference by $Ca^{2+}$, $Mg^{2+}$, and $Zn^{2+}$.

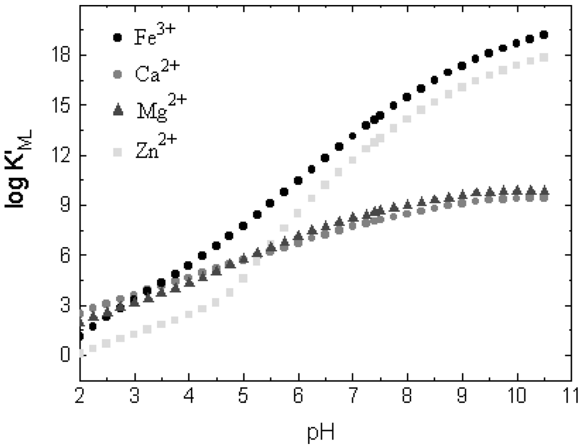

**FIGURE 4** Variation of the conditional stability constants for $Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, and $Fe^{3+}$ complexes with EDTMP with pH.

The pH dependence of the conditional stability constants for the 1:1 complexes of $Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, and $Fe^{3+}$ with EDTMP is given in Figure 4. It is observed that for the entire pH domain $\log K'_{FeL} > \log K'_{ZnL}$; however, for the pairs $\log K'_{FeL} - \log K'_{CaL}$ and $\log K'_{FeL} - \log K'_{MgL}$, there is the same inequality at pH > 3.5.

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