Complex formation equilibria in iron(III)-L-alanine system

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Summary

Complex formation in iron(III)-L-alanine solutions was studied by emf glass electrode and spectrophotometric measurements, in 0.5 mol dm^{-3} (Na)NO_3 medium, at 25° C. In the concentration range $0.5 \leqslant [Fe]_0 \leqslant 20.0$, $5.0 \leqslant [Ala]_0 \leqslant 1000.0$ (mmol dm^{-3}) and $1.0 \leqslant -\log [H^+] \leqslant 3.5$; $\{[Ala]/[Fe] = 10:1–100:1\}$ the equilibria in the title system were explained by the model including the species FeHL, FeL, Fe(OH)L, $Fe_2(OH)_2L_2$ (where HL denotes L-alanine) and several hydrolytic products. The stability constants of complexes are given. The mechanism of formation and structure of complexes in solution is proposed.

Introduction

In our earlier paper[1] it was established that in iron(III)-glycine solutions the formation of $[FeGly]^{2+}$ complex becomes dominant at concentration ratio $[Gly]/[Fe] \geqslant 50$ and pH $\geqslant 2.5$. Extending these investigations to the other Fe^{III}-amino acid systems, in this work the stability constants of iron(III)-L-alanine complexes are determined under the similar experimental conditions.

The knowledge of complex formation equilibria of Fe^{III} with L-alanine (Ala)† is relevant in understanding its possible interactions with likely biological ligands. So far only a few studies on the iron(III)-alanine system have been reported. Redox potentiometric measurements have been made by Perrin[2] who found the $[FeAla]^{2+}$ complex to possess a stability constant $\log \beta_{1,0,1} = 10.4$. Redox potentiometry was also employed by Shcherbakova *et al.*[3]. At an alanine to iron concentration ratio of 100:1 they identified $[Fe(HAla)_2]^{3+}$ and $[Fe_2(HAla)_2Ala_2]^{4+}$ complexes. The stability constant of $[FeAla]^{2+}$ complex was determined polarographically ($\log \beta_{1,0,1} = 10.98$) by Kapoor and Mathur[4].

The existing data are rather discordant in view of the existence of [FeHAla] and other mixed complexes, which may be formed in solution. Therefore, the objective of the present work was to find the best complex formation model in the iron(III)-alanine system as well as to determine the stability constants of the species formed in solution, with the emphasis on ternary species. The measurements were made in 0.5 mol dm^{-3} (Na)NO_3 medium at 25° C using glass electrode potentiometric and spectrophotometric measurements. The notation of the medium is in accordance with Sillen and Martel[5]. Relatively high concentration ratios of alanine to Fe^{III} (10:1, 20:1, 30:1, 50:1 and 100:1) were employed since the complex formation is disturbed in a considerable extent by the pronounced hydrolysis of iron(III) ion. The hydrolytic polymerization of Fe^{III} aqua ion was taken into account on the basis of our previous work[6]. Owing to extensive degree of hydrolysis at higher pH values and the formation of various hydrolytic precipitates, the pH range was restricted to below pH *ca.* 3.5, so that the influence of hydrolysis on the complex formation could be minimized.

Experimental

Reagents

All chemicals used were of analytical grade purity. H_2O was doubly distilled. The stock solution of iron(III)-nitrate was prepared by dissolving Fe powder (Merck) in 1:1 HNO_3 and analyzed as described previously[1]. The stock solution of alanine (Merck) was standardized by titration with NaOH. HNO_3 "Suprapur" (Merck) was standardized against $(HOCH_2)_3CNH_2$. Carbonate-free NaOH was standardized against potassium hydrogenphthalate using a Gran plot. The stock solution of $NaNO_3$ was prepared by dissolving twice recrystallized $NaNO_3$ (Merck) in H_2O. The concentration was determined by evaporation of known volume of solution to dryness at 150° C and weighing the residue.

Apparatus and procedure

Potentiometric measurements were made on solutions in a double-walled glass vessel at (25.0 ± 0.1)° C, with a commercial Beckman (39501 B8U) combined electrode. The emf was measured with a Beckman Model 4500 digital pH-meter with a precision of ±0.1 mV. The temperature was controlled by circulation of water through the jacket, from a VEB model E3E ultrathermostat bath and maintained within ±0.1° C. The room was also thermostatted at (25 ± 1)° C. Purified nitrogen gas was bubbled through solution, which was vigorously stirred with magnetic stirrer. All test solutions were prepared in a constant ionic medium, 0.5 mol dm^{-3} (Na)NO_3 by mixing the appropriate amounts of Fe^{III}, HNO_3, L-alanine and $NaNO_3$ solutions. The general composition of the test solutions was: TS = MFe^{III}, H, H^+, CL-Ala, 0.5 mol dm^{-3} NO_3^-. The Na^+ concentration is omitted for simplicity. In another series of titrations the acidified solution of Fe^{III} ion was titrated with sodium alaninate, which was prepared by neutralization of L-alanine with equimolar quantity of NaOH. All test solutions were allowed to stand one month before commencing the titrations.

The concentration of hydrogen ion was decreased by the addition of NaOH or sodium alaninate which were prepared in the same ionic medium as used for the test solutions. The base was delivered using Metrohm Dosimat Model 665 equipped with Exchange unit Model 552. During the titrations the solutions were monitored for the appearance of the turbidity or precipitate. As soon as the formation of insoluble species started, as indicated by drifting potential readings, the titrations were terminated. The concentration of free hydrogen ion, $[H^+]$, at each point of titration was calculated from the measured emf, E, of the cell from the Nernst formula:

$$E = E_0 + Q \log [H^+] \quad (1)$$

where E_0 is a constant which includes the standard poten-

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† Abbreviations: alaninate ion, Ala; alanine (zwitterion), HAla; alanine (neutral), AlaH; alanine cation, H_2Ala^+.

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tial of the glass electrode and Q is the slope of the glass electrode response. The E_0 was determined both, before and during each titration of the test solutions. First, E_0 was determined by means of separate titration of diluted nitric acid (1.0, 2.5 and 5.0 mmol dm^{-3}) with 0.085 mol dm^{-3} NaOH under the same medium and temperature conditions as for the test solution titrations. The data so obtained were analyzed by the Magec program[7]. During the Magec calculations the auto protolysis constant of water, K_w was refined until the best value for Q was obtained. The value of Q at 25° C was found to be 58.9 mV and that for the autoprotolysis constant, $pK_w = 13.76(5)$. The results obtained indicate the reversible Nernstian response of glass electrode used. These values were used in all subsequent calculations. During the titrations of the test solutions the E_0 was determined using the data in acidic region, where no hydrolysis or complex formation takes place, by plotting the value $E - Q \log [H^+]$ versus $[H^+]$ and extrapolating the straight line so obtained to $[H^+] = 0$. When the difference between the refined and extrapolated E_0 was greater than 2.0 mV the titration was rejected.

The spectrophotometric measurements were performed with a Varian Super Scan 3 U.v.–vis. spectrophotometer at room temperature (ca. 25° C). Quartz cells of path length 1.0 cm (matching pairs) were used, the reference cell being filled with the corresponding iron-free solutions.

Computational procedure

Three kinds of equilibria must be considered in the present study: (a) protonation of alaninate ion, (b) hydrolysis of iron(III) ion and (c) general three-component complex formation equilibria. For the protonation equilibria of alaninate ion (here and afterwards the charges of complexes are omitted for the sake of clarity):

$$nH + Ala \rightleftarrows H_nAla \quad (n = 1, 2);\ \beta_{0,1,1} \text{ and } \beta_{0,2,1}$$

the values of corresponding constants ($\log \beta_{0,1,1} = 9.63$, $\log \beta_{0,2,1} = 12.07$) were taken from our previous work[8]. For the hydrolytic equilibria of Fe^{III}:

$$pFe + qH_2O \rightleftarrows [Fe_p(OH)_q] + qH^+;\ \beta_{p,-q,0}$$

the results obtained in the earlier papers[1,6] for the hydrolytic complexes of iron, [FeOH] ($\log \beta_{1,-1} = -2.58$), $[Fe_2(OH)_2]$ ($\log \beta_{2,-2} = -3.15$), $[Fe(OH)_2]$ ($\log \beta_{1,-2} = -6.36$) were used. In evaluation of three component equilibria (including q = 0):

$$pFe + qH + rAla \rightleftarrows [Fe_pH_q(Ala)_r];\ \beta_{p,q,r}$$

these binary models were considered as known. Thus, all the effects above (a) and (b) were considered as being caused by three-component or binary alaninato-iron(III) species.

The mathematical analysis of data was performed with non-linear least-squares programs Superquad[9] and Squad[10]. In Superquad calculations of potentiometric data composition and stability constants of complexes that best fit the experimental data were determined by minimizing the error-square sum, U, of potentials:

$$U = \sum w_i (E_{obs} - E_{calc})^2 \quad (2)$$

where E_{obs} and E_{calc} refer to measured potential and that calculated from Equation 1 assuming the specific model and the corresponding estimates of the stability constants. w_i denotes statistical weight assigned to each point of the titration curve. In Squad calculations of the spectral data, the composition, stability constants and molar absorptivities, $\varepsilon_{p,q,r}$ of complexes were determined by minimizing the sum S, defined as:

$$S = \sum (A_{obs} - A_{calc})^2 \quad (3)$$

where A_{obs} and A_{calc} refer to measured absorbance and that calculated from Equation 4:

$$A_{calc} = \sum \beta_{p,q,r} [Fe]^p [H]^q [Ala]^r \varepsilon_{p,q,r} \quad (4)$$

All the calculations were performed on an IBM PC AT-386/25 compatible computer.

Results

Potentiometric measurements

The composition of the solutions used for potentiometric measurements are presented in Table 1.

Establishing of equilibria in these systems was relatively slow. NaOH was added every 20 min.; potential readings being taken every 5 min until stable values, within ±0.2 mV, were obtained. Thus, the rapidly formed species can reach the concentration suitable for potentiometric measurements, without allowing, in the same time, the significant interference from the slow formation of higher polynuclear hydrolytic complexes. In this way the potentiometric measurements were actually performed on metastable states of the system. Deep red colour was developed during the titrations; eventually solution became turbid and precipitation occurred (pH ca. 3.7). At this point titration was discontinued. At pH values higher than ca. 3.0 solutions might become unstable with regard to separation of colloid phase. Therefore, the titrations were stopped at some definite point, near pH ca. 3.0 and solutions were left to stand for another 24 h under the slow stream of nitrogen. The titrations were resumed only if no turbidity or precipitation occurred, within the specified period of time, otherwise the solutions were discarded. Plot of the pH versus the titration parameter, a* shows that the pH rises steeply with the addition of base, with small inflexion near a ca. −0.2. The titration curves referring to different initial concentrations of iron, coincide at $a > -0.5$, within experimental errors thus, indicating the formation of

Table 1. Summary of the potentiometric data obtained in the iron(III)-L-alanine solutions in 0.5 mol dm^{-3} $(Na)NO_3$ medium at 25° C. C_x denotes initial total concentration of corresponding species in mmol dm^{-3}.

Entry	C_{Fe}	C_{HNO_3}	C_{Ala}	pH range	No. of points
1	0.50	9.92	5.26	2.164–3.359	160
3	1.00	15.06	10.52	2.089–3.651	163
4	1.20	43.00	11.79	1.471–3.123	86
5	2.60	45.94	24.56	1.573–2.642	130
6	5.00	51.05	49.13	1.885–2.575	67
7	10.00	61.71	98.27	1.961–2.525	87
8	1.20	42.96	24.56	1.556–2.720	97
9	2.60	45.94	49.16	1.989–2.925	81
10	5.00	50.95	98.30	2.156–2.700	64

* The titration parameter was calculated as (mmoles of base added − mmoles of HNO_3)/mmoles of Ala. Negative values of a denote excess of strong acid.

mononuclear complexes. The general shape of the titration curves obtained, demonstrates extensive hydrolysis in the system. In the data analysis the pH range was restricted between 1.4 and 3.0 pH units. Points below pH 1.4 were excluded since the complexation, owing to low concentration of the alaninate ion, is negligible. Beyond pH ca. 3.1 hydrolysis is so extensive that the formation of colloidal phase may take place. Approximately 80 points per titration were used in calculations. 300 points were included in Superquad calculations at each particular alanine to iron concentration ratio (10:1 and 20:1). The following complexes and their combinations were tested during the calculations: monomeric, (1,0,1), (1,0,2), (1,1,1), (1,1,2), (1,−1,1), (1,2,2), (1,−2,1); polymeric, (2,0,2), (2,0,3), (2,2,4), (2,2,2), (2,−2,2), (2,2,3), (2,−2,1), (2,−2,4), (3,−2,6), (3,−3,3), (3,0,4). The calculations were carried out in the way described by Gillard *et al.*[11]: starting from the "base" model (1,0,1), (1,1,1), (1,−1,1), (2,−2,1) first each titration curve was treated separately, adding or removing complexes in a systematic manner. All the complexes found in such a way were used as the initial model in Superquad calculation of the data pertaining to all curves referred to one definite concentration ratio [Ala]/[Fe]. First, only the points from the initial part of the titration curves, between pH 1.4 and 2.0, were taken into account. The Superquad calculations with these points indicated the formation of [FeHAla] complex only, with the stability constant $\log \beta_{1,1,1} = 11.01 \pm 0.03$. Taking $\beta_{1,1,1}$ as known constant the Superquad program was used to calculate the $\beta_{p,q,r}$ of other species, now including all titration points, up to pH ca. 3.0. The data treatment indicates the formation of [Fe(OH)Ala] complex at all the concentration ratios [Ala]/[Fe] employed, with a stability constant $\log \beta_{1,-1,1} = 6.63 \pm 0.03$. At the concentration ratio 20:1 besides the mixed complexes the evidence was found for the formation of [FeAla] complex. Inclusion of this complex in the model required the refinement of the stability constants of the pure hydrolytic complexes of iron. The complex (1,−2,0) was rejected and the stability constants of (1,−1,0) and (2,−2,0) complexes, changed for ca. 1%. The stability constant of [FeAla] was found to be $\log \beta_{1,0,1} = 9.1 \pm 0.17$. The calculated standard deviation in stability constant of [FeAla] was rather high. It may be attributed to the insufficiently high ratio [Ala]/[Fe] to produce adequate concentration of [FeAla] complex for potentiometric detection. Since, however, the concentration ratio [Ala]/[Fe], can not be further increased without considerable alteration of the medium, as well as the influence of buffer effect of the ligand protonation on the accuracy of the measurements, the several titrations were made in such a way that the solutions of Fe^{III} ion (0.5, 1.0 and 2.0 mM) were titrated with sodium alaninate solution (0.104 M). At the end of the titration the pH was ca. 3.3 and the concentration ratio [Ala]/[Fe] ca. 30:1. In the data treatment only the points between pH 2.3 and 3.0 were included. Calculations involving the refinement of $\beta_{1,0,1}$ (with $\beta_{1,1,1}$ held constant) gave the result $\log \beta_{1,0,1} = 8.80 \pm 0.09$. Inclusion of minor species (2,−2,2) and (2,−1,2) did not improve the fit. Thus, it may be concluded that the model consisting of [FeHAla], [FeAla] and [Fe(OH)Ala] complexes, as well as pure hydrolytic complexes, gives a satisfactorily good fit to the potentiometric data. The statistical parameters, which determine the goodness of fit[9], were: standard deviation in potential residuals, s, between 3.1 and 5.0 and χ^2 between 12.0 and 26.0, in different sets of titration curves. Plot of the distribution of potential residuals versus pH, showed slight systematic trend, especially at pH > 2.8. Somewhat higher values of statistics, than desirable may be attributed to the fact that the solutions are actually in metastable state with respect to the formation of pure hydrolytic species of iron. It means that various transient species may coexist in solution, for some period of time, causing unstable, slowly drifting, potential readings. This gives rise to the uncertainty of the composition and stability of the species formed in solution. The formation of pure alaninato-Fe^{III} complex, [FeAla], starts at pH 1.5 while the formation of mixed hydrolytic complex, [Fe(OH)Ala] starts at pH 1.9 and sharply increases with increasing the pH. The protonated complex, [Fe(HAla)] begins to form at considerably lower pH values (ca. 1.2) and reaches the maximum concentration at pH ca. 2.0.

Spectrophotometric measurements

The composition of the solutions used in spectral measurements are presented in Table 2.

The pH of the test solutions was measured in an electrochemical cell equipped with glass/calomel electrode couple, calibrated with a series of standard solutions of nitric acid (0.50, 1.00, and 5.00 mmol dm^{-3}) in 0.5 M $(Na)NO_3$. All test solutions were allowed to stand 10 days before measurements were made. The pH of solutions was recorded daily. The stable values, within 0.02 pH units, were attained after few days and remained constant for several days. Spectra of the solutions were recorded in 400–600 nm wavelength interval. For the purpose of the Squad calculations, the spectra were digitized at every 5 nm. The spectra exhibit a band in 440–470 nm region centred at 460 nm. The plateau exists between 500 and 530 nm. The dependence of the intensity and position of the band and plateau upon pH, indicates the presence of the several complexes.

In Squad calculations, of the spectral data, the extinction coefficient of aqua-Fe^{III} was set to zero, while the extinction coefficients of [FeOH] and $[Fe_2(OH)_2]$ were taken from our previous work[6]. The calculations were performed first by using the multiple linear regression option adding the complexes one at a time until the lowest values for standard deviations in calculated constants were obtained. Then, the final refinement of calculated constants and

Table 2. Summary of spectrophotometric data in iron(III)-L-alanine solutions. C_x denotes total concentration of corresponding species in mol dm^{-3}.

Entry	C_{Fe}	C_{Ala}	pH
1	0.010	0.500	0.976
2	0.010	0.500	1.816
3	0.010	0.500	2.397
4	0.010	0.500	3.042
5	0.010	1.001	1.215
6	0.010	1.002	1.558
7	0.010	1.002	1.733
8	0.010	1.001	2.198
9	0.010	1.002	2.391
10	0.010	1.002	2.707
11	0.010	1.002	2.897
12	0.010	1.002	3.302
13	0.010	1.002	3.650
14	0.020	1.002	2.343
15	0.020	1.002	3.224
16	0.005	0.250	2.960

extinction coefficients was performed with non-linear least squares option of Squad. The results of calculations indicate that the experimental data, referring to 100:1 [Ala]/[Fe] concentration ratio, can be explained by assuming the formation of [FeHAla], [FeAla] and [Fe(OH)Ala] complexes with the stability constants, $\log \beta_{1,1,1} = 10.41 \pm 0.01$, $\log \beta_{1,0,1} = 8.96 \pm 0.10$ and $\log \beta_{1,-1,1} = 6.29 \pm 0.08$ respectively. At 50:1 [Ala]/[Fe] ratio it was necessary to include the (2,−2,2) complex, with a stability constant $\log \beta_{2,-2,2} = 10.91 \pm 0.08$, as minor species, in order to achieve acceptable fit. The statistical parameters of fit[10] were: the standard deviation in absorbance data, SD, between 8.0×10^{-4} and 1.2×10^{-3}, and S (Equation 3) was between 3.0×10^{-3} and 8.2×10^{-3}. On the basis of these values the fit may be considered as adequate, bearing in mind that various transient hydrolytic complexes of iron at the pH values examined, may be present in solutions. Calculated spectrum of [FeAla] complex shows the monotonical decrease of extinction with increasing the wavelength with a small band centred at 455 nm.

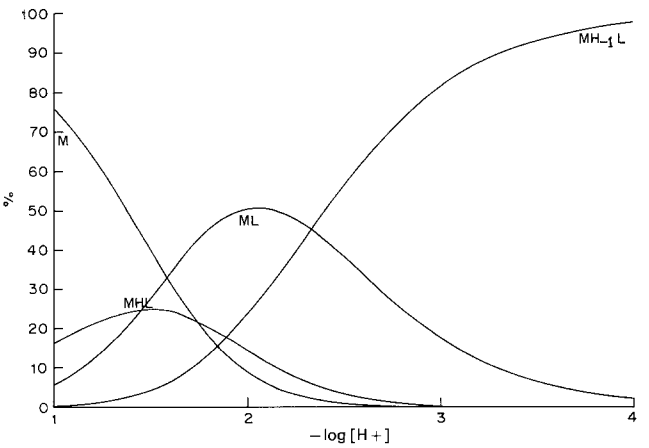

Figure 1. Percentage distribution of the species formed in iron(III)-L-alanine solutions in 0.5 M $(Na)NO_3$ medium, at 298 K. Concentration of Fe^{III} is 10 mmol dm^{-3} and that of alanine 1 mol dm^{-3}. Distribution was calculated with the aid of programs SPE and SPEPLOT[12]. The labels denote: M = Fe, L = Ala.

Discussion

The distribution diagram of the species formed in solution is shown in Figure 1.

Pure hydrolytic species are not shown since their contribution to overall distribution was less than 5%. The dominating complexes in the 2.1–3.0 pH range are [FeAla] and [Fe(OH)Ala] while at lower pH values the formation of [Fe(HAla)] complex is significant.

Comparison of spectrophotometric with potentiometric data shows fairly good agreement with somewhat wider range of values of stability constant. This is not surprising bearing in mind different concentration ranges employed as well as the fact that spectral measurements were made in nearly true equilibrium conditions while the potentiometric measurements were performed, owing to slow establishment of equilibrium, in metastable conditions. The values of the stability constants obtained in Squad calculations may be considered as preferable to those obtained in Superquad calculations owing to better set of statistics of the fit.

It may be supposed that in [FeHAla] complex the alanine is coordinated to iron only through carboxyl oxygen atom, while nitrogen does not participate in coordination, since the same mode of coordination was found in $[Fe^{II}(HAla)_2]$ complex[13] by X-ray structure determination. This conclusion is further supported by comparison of the stability constant of acetato–Fe^{III} complex, [FeAc] ($\log \beta = 3.5$)[5] with the stability constant of [Fe(HAla)], K, defined as:

$$K = [FeHAla]/[Fe][HAla] \quad (5)$$

and calculated using the Martin's equation[14]:

$$\log K = \log \beta_{1,1,1} - 0.7 \times \log \beta_{0,1,1} \quad (6)$$

$$\log K = 3.4$$

Since acetate is coordinated to iron only through carboxyl oxygen[15], then similar values of the constants obtained indicate the same mode of coordination of HAla.

The mixed hydrolytic complex, [Fe(OH)Ala], may be formed by several mechanisms, of which the hydrolysis of [FeAla]:

$$[FeAla] + H_2O \rightleftarrows [Fe(OH)Ala] + H^+ \quad (7)$$

seems the most probable at high concentrations of alanine (1 M) and pH > 2.5. At lower pH values, where the concentration of [Fe(OH)] is significant, the mixed complex may be formed by attaching the alaninate ion to hydrolytic monomer according to reaction:

$$[FeOH]^{2+} + Ala^- \rightleftarrows [Fe(OH)Ala] \quad (8)$$

The equilibrium constant, $\log K_{1,a}$ of the reaction represented by Equation 7, is:

$$\log K_{1,a} = \log \beta_{1,-1,1} - \log \beta_{1,0,1}$$
$$\log K_{1,a} = 6.29 - 8.96 = -2.67 \quad (9)$$

and is very close to the first hydrolytic constant of the aqua-iron(III) ion itself (−2.58). It follows therefore, that the coordination of alanine to iron has only a slight effect on the protolysis of water molecule, coordinated to iron.

Considering the concentrations of the species formed in solution from the distribution diagram (Figure 1), one may devise the following reaction path for the formation of the [FeAla] complex:

$$Fe^{3+} \rightarrow [FeOH] \rightarrow [Fe(OH)HAla] \rightarrow [FeAla]$$

A similar path was proposed[16] for the formation of [FeGly] complex. In the acidic solutions, the transient species [Fe(OH)HAla] may be formed either by attaching the alanine zwitter ion, HAla to the first hydrolytic product of iron, [FeOH], or by protolysis of water molecule coordinated to iron in [FeHAla] complex. This species is metastable and may exist in solution over prolonged period of time. In equilibrium calculations the complex [Fe(OH)HAla] can not be differentiated from [FeAla]. It explains rather high uncertainty in calculated stability constant of [FeAla]. The alanine in [Fe(OH)HAla] is coordinated to iron only through carboxyl oxygen, similarly as in [Fe(OH)HGly][1]. Owing to high affinity of iron to hydroxyl group[17] the splitting of water molecule off from [Fe(OH)HAla] may proceed slowly and perhaps, not in high extent.

Another way of formation of [FeAla] may be the protolytic dissociation of [FeHAla]. The extent of dissociation increases with increasing the pH, as evidenced from the distribution diagram in Figure 1. This reaction may be followed by closing up the five-membered glycine-like ring, so that [FeAla] possesses the chelate structure[18]. The stability constant of [FeAla] is only slightly higher

than that of [FeGly] (8.96 versus 8.57) thus, reflecting relatively small + I effect of CH_3 group on alanine carboxyl oxygen. The value for the stability constant of [FeAla], obtained in this work, is considerably smaller than those obtained by other authors[2–4]. Also, the formation of *bis*- and higher alaninato complexes was not observed in our work as opposed to the observations of some authors[18]. The differences are attributable to different equilibration procedure and concentration ranges employed.

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