

Thermodynamic investigation of the binary and ternary complexes involving 1-aminocyclopropane carboxylic acid with reference to plant hormone

Research Article

Mohamed M. Shoukry^{1,2*}, Safaa S. Hassan²

¹Department of Chemistry, Faculty of Science, Islamic University, 170 Madina, Kingdom of Saudi Arabia

²Department of Chemistry, Faculty of Science, University of Cairo, 12613 Cairo, Egypt

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Abstract: Complex formation equilibria of 1-aminocyclopropane carboxylic acid (ACC) and 3,3-bis(1-methylimidazol-2-yl) propionic acid (BIMP) with metal ions Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} and Fe^{2+} were investigated. ACC forms 1:1 and 1:2 complexes in addition to the hydrolysed form of the 1:1 complex, except in the case of Mn^{2+} and Fe^{2+} , where the hydrolysed complex is not formed. BIMP forms 1:1 and 1:2 complexes in addition to the hydrolysed form of the 1:1 complex in the case of Mn^{2+} and Cu^{2+} , however the hydrolysed complex is not detected for Ni^{2+} , Co^{2+} , Zn^{2+} and Fe^{2+} . The concentration distribution diagrams of the complexes were determined. The Fe^{2+} complex with BIMP is exothermic and the thermodynamic parameters were calculated. The effect of organic solvent on the acid dissociation constants of 1-aminocyclopropane carboxylic acid (ACC) and 3,3-bis(1-methylimidazol-2-yl) propionic acid (BIMP) and the formation constants of Fe^{2+} complexes were investigated. Fe^{2+} forms a mixed-ligand complex with ACC and BIMP with stoichiometric coefficients 1:1:1. The formation constant was determined. The ternary complex is enhanced by back donation from the negatively charged 1-aminocyclopropane carboxylate to the π -system of BIMP. From the concentration distribution diagram, the ternary complex prevails in the physiological pH range.

Keywords: 3,3-bis(1-methylimidazol-yl)propionic acid • 1-aminocyclopropane carboxylic acid • Equilibrium studies • Plant hormone
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1. Introduction

The plant signaling molecule ethylene is involved in a diverse range of physiological processes, including regulation of plant growth/development, fruit ripening and in responses to pathogen infection and mechanical wounding [1-4]. Ethylene is found in most plant tissues and is biosynthesised from 1-aminocyclopropane carboxylic acid (ACC) using ACC oxidase (ACCO). ACCO is known as the ethylene-forming enzyme. The crystallographic structure of ACCO from *Petunia hybrida* that was recently resolved reveals that it is a member of an iron(II) complex involving a nitrogenous ligand with imidazole and carboxylate groups as enzyme active sites [5]. Parallel to the discovery of ACC to be the direct precursor of the plant hormone ethylene, it was

shown that 1-aminocyclopropane carboxylic acid and numerous derivatives thereof exhibit herbicidal activity and influence plant growth, caused by intervention in metabolism [6]. In addition, very small amounts of ACC bring about body weight gain and promotion of protein synthesis in microorganisms and animals [7].

Work in our laboratories has focused on metal complexes of biological significance [8-15]. It is of considerable interest to study some transition metal ion complexes involving 1-aminocyclopropane carboxylic acid (ACC) and 3,3-bis(1-methylimidazol-2-yl)propionic acid (BIMP) having two imidazole and one carboxylate groups, taken as a model of ACCO. Also, in the present study, the ternary complexes of iron(II) with ACC and BIMP are investigated. The formation constants of the complexes formed in solution at different temperatures

* E-mail: shoukrymm@hotmail.com

and in dioxane-water solutions of different compositions are determined. The results of this investigation will support the biological significance of this class of complexes.

2. Experimental procedure

2.1. Materials and reagents

1-aminocyclopropane carboxylic acid (ACC) was provided by Sigma Chem. 3,3-bis(1-methylimidazol-2-yl)propionic acid (BIMP) was prepared as a sodium salt as described previously [16]. BIMP was prepared in the protonated form with standard HNO₃ solution. Dioxane was provided by Aldrich Chem. Co. FeSO₄ salt and the other metal salts in the form of nitrates were provided by BDH. The metal ion content of solutions was determined by complexometric EDTA titrations [17]. Carbonate-free NaOH (titrant) was prepared and standardized against potassium hydrogen phthalate solution. All solutions were prepared in deionized H₂O.

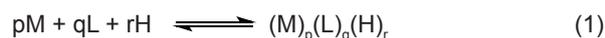
2.2. Apparatus and measuring techniques

Potentiometric measurements were made using a Metrohm 686 titroprocessor equipped with a 665 Dosimat (Switzerland-Herisau). The titroprocessor and electrode were calibrated with standard buffer solutions, prepared according to NBS specifications [18]. All titrations were carried out at 25 ± 0.1°C, in a double-walled glass cell, through the outer jacket of which water was circulated from a constant temperature bath.

2.3. Equilibrium studies

The acid dissociation constants of the ligands were determined potentiometrically by titrating the ligand solution (40 cm³ at a concentration of 2.5×10⁻³ M) of constant ionic strength of 0.1M, adjusted with NaNO₃. The stability constants of the binary complexes were determined by titrating 40 cm³ of a solution mixture of metal ion (1.25×10⁻³ M), the ligand (2.5×10⁻³ M) and NaNO₃ (0.1 M). The stability constant of the Fe²⁺ ternary complex was determined by titrating the solution mixture (40 cm³) of Fe²⁺, ACC and BIMP in concentration ratios of 1:1:1, each of concentration 1.25×10⁻³ M. The concentration of NaNO₃ in the mixture was 0.1 M. All titrations were performed in a purified N₂ atmosphere, using aqueous 0.05 M NaOH (in 0.1 M NaNO₃).

The general three component equilibrium can be written as follows (charges are omitted for simplicity):



for which the formation constants are given by

$$\beta_{pqr} = \frac{[(M)_p(L)_q(H)_r]}{[M]^p [L]^q [H]^r}$$

Calculations were performed using the computer program MINQUAD-75 [19] on an IBM computer. The model selected was that which gave the best statistical fit and which was chemically consistent with the titration data without any system bias in its residuals [19]. The results obtained are listed in Tables 1-6. The concentration distribution diagrams were obtained using the program SPECIES (L.Pettit, Personal communication) under the experimental conditions described.

3. Results and discussion

3.1. Binary complexes

The ligand titration curve in the presence and absence of the metal ions (Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Mn²⁺ and Fe²⁺) are compared. The metal-ligand titration curves lie below the ligand curve, which can be attributed to the liberation of proton(s) through displacement by the metal ions during complex formation. The potentiometric data of ACC complexes provide a good fit assuming the formation of 1:1 and 1:2 complexes in addition to the hydrolysed form of the 1:1 complex (11-1). The exceptions to this are Mn²⁺ and Fe²⁺, where the hydrolysed complex is not formed, most probably due to its insolubility as a result of electrical neutrality. BIMP forms 1:1 and 1:2 complexes in addition to the hydrolysed form of the 1:1 complex in the cases of Mn²⁺ and Cu²⁺. However, the hydrolysed complex is not detected with Ni²⁺, Co²⁺, Zn²⁺ and Fe²⁺ ions, most probably due to the insolubility of the hydrolysed species. The formation constants of the complexes are given in Tables 1 and 2. It was found that (log K₁ – log K₂) values are usually positive, since the coordination sites of the metal ions are more readily available for binding of the first ligand as compared to the second [20-22].

Estimation of the concentration distribution of the complex species in solution provides a useful picture of metal ion binding. The main features observed in the species distribution plots in these systems are shown in the speciation diagram obtained for the Zn(II)–ACC complex, taken as a representative example and given in Fig. 1. The 1:1 complex starts to form at pH 4.0 and reaches the maximum concentration of 62% at pH 6.7. At higher pH, the concentration of the 1:1 complex decreases and the 1:2 complex concentration increases, attaining the maximum degree of formation of 20% at pH 8.0. The hydrolysed complex species starts to form at pH 6 and its concentration increases with increasing pH.

Table 1. Formation constants of 1-aminocyclopropane carboxylic acid complexes of the general formula $M_p(ACC)_qH_r$ at 25°C and 0.1 M ionic strength.

System	p q r	Log β^a
Cu-ACC	1 1 0	7.78 (0.01)
	1 2 0	14.42 (0.01)
	1 1 -1	1.47 (0.01)
Ni-ACC	1 1 0	5.41 (0.01)
	1 2 0	10.04 (0.01)
	1 1 -1	-2.93 (0.02)
Zn-ACC	1 1 0	4.66 (0.01)
	1 2 0	7.98 (0.05)
	1 1 -1	-3.06 (0.02)
Co-ACC	1 1 0	4.44 (0.03)
	1 2 0	7.77 (0.04)
	1 1 -1	-4.36 (0.03)
Mn-ACC	1 1 0	2.19 (0.12)
	1 2 0	5.40 (0.04)
Fe-ACC	1 1 0	6.38(0.1)
	1 2 0	10.72(0.1)

^a Standard deviation is given in parentheses

Table 2. Formation constants of metal complexes with BIMP complexes of general formula $M_p(BIMP)_qH_r$ at 25°C and 0.1 M $NaNO_3$.

System	p q r	Log β
Cu- BIMP	1 1 0	9.92 (0.01)
	1 2 0	17.08 (0.03)
	1-1 1	6.66 (0.01)
Ni- BIMP	1 1 0	8.17 (0.01)
	1 2 0	14.46 (0.02)
Co- BIMP	1 1 0	6.57 (0.02)
	1 2 0	11.36 (0.05)
Zn- BIMP	1 1 0	6.27 (0.01)
	1 2 0	11.08 (0.01)
Mn- BIMP	1 1 0	3.89 (0.03)
	1 2 0	6.98 (0.04)
	1 1 -1	-5.22 (0.07)
Fe-BIMP	1 1 0	6.07(0.05)
	1 2 0	10.2(0.05)

3.2. Effect of temperature

3,3-bis(1-methylimidazol-2-yl)propionic acid protonation constants were determined by direct potentiometric pH measurements because all protonation reactions were observed to take place within the potentiometrically measurable pH range. Protonated 3,3-bis(1-methylimidazol-2-yl)propionate behaves as triprotic acid (H_3A^{2+}), where the differential log protonation constants were found to be 2.19, 4.20 and 7.11 at 25°C. The first constant corresponds to the carboxylic group and the second and third constants correspond to the protonated imidazole groups.

The values obtained for the thermodynamic parameters ΔH° and ΔS° associated with protonation

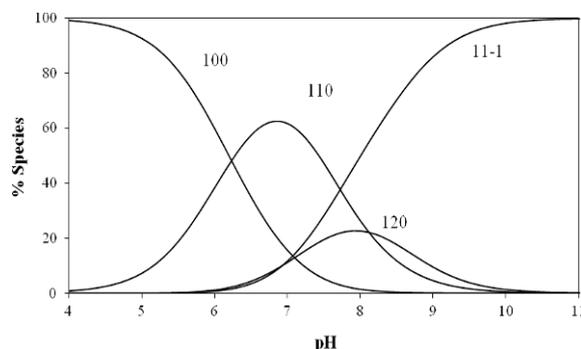


Figure 1. Concentration distribution diagram of Zn(II)-1-aminocyclopropane carboxylic acid complexes at 25°C.

of 3,3-bis(1-methylimidazol-2-yl)propionic acid and its complex formation with Fe^{2+} were calculated from the temperature dependence of the data in Table 3. The thermodynamic parameters ΔH° and ΔS° were obtained by a linear least square fit of $\ln K$ versus $1/T$ ($\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R$) leading to an intercept at $\Delta S^\circ/R$ and a slope of $-\Delta H^\circ/R$. The results are summarized in Table 4 and can be interpreted as follows:

- The protonation reactions of (BIMP) (Reactions 1-3, Table 6) are exothermic ($\Delta H^\circ = -22.15, -14.43$ and $-11.92 \text{ kJ mol}^{-1}$), as expected for neutralization reactions.

The stability constants of the complexes formed at different temperatures (Reactions 4, 5 in Table 4) lead to the following conclusions:

- The formation of FeA^+ and FeA_2 complexes is exothermic; A negative ΔH° and a positive ΔS° leading to a negative ΔG° for the complexation reaction indicate the spontaneity of the chelation process.

- The positive entropy changes indicate a release of ordered water molecules and the breaking of hydrogen bonds.

- The negative values of ΔH° in reactions show that the chelation process is exothermic, indicating that the complexation reactions are favored at low temperatures.

3.3. Effect of solvent

In order to examine the effect of organic solvent upon Fe^{2+} complexes with 1-aminocyclopropane carboxylic acid and 3,3-bis(1-methylimidazol-2-yl)propionate, the corresponding stability constants were determined in various dioxane/water mixed solvents. As a reference, the acid dissociation of 1-aminocyclopropane carboxylic acid 3,3-bis(1-methylimidazol-2-yl)propionate in the same solvent was also studied. The dioxane-water mixture is an interesting binary mixture as it represents a model for a biological fluid. In enzyme-containing solutions, membranes and other biologically important media, the equilibrium constants of bio-ligands are very different from those in water, as these media

Table 3. Formation constants of Fe(II)-BIMP complexes of general formula $Fe_p(BIMP)_qH_r$ in aqueous solution at different temperature and ionic strength 0.1 M $NaNO_3$.

System	T°C	p	q	r ^a	Log β^b	pK _a
Fe- BIMP	15	0	1	1	7.23(0.01)	7.23
		0	1	2	11.51(0.01)	4.28
		0	1	3	13.89(0.02)	2.38
		1	1	0	6.14(0.02)	
		1	2	0	10.34(0.04)	
Fe- BIMP	20	0	1	1	7.19(0.01)	7.19
		0	1	2	11.43(0.02)	4.24
		0	1	3	13.71(0.03)	2.28
		1	1	0	6.09(0.01)	
		1	2	0	10.27(0.01)	
Fe- BIMP	25	0	1	1	7.11(0.01)	7.11
		0	1	2	11.31(0.02)	4.20
		0	1	3	13.50(0.03)	2.19
		1	1	0	6.07(0.05)	
		1	2	0	10.2(0.05)	
Fe- BIMP	30	0	1	1	7.04(0.01)	7.04
		0	1	2	11.19(0.02)	4.15
		0	1	3	13.43(0.02)	2.24
		1	1	0	6.06(0.02)	
		1	2	0	10.13(0.04)	
Fe- BIMP	35	0	1	1	6.97(0.01)	6.97
		0	1	2	11.09(0.05)	4.12
		0	1	3	13.32(0.02)	2.23
		1	1	0	6.05(0.01)	
		1	2	0	10.11(0.04)	

Table 4. Thermodynamic parameters for the equilibria of Fe^{2+} complexes with 3,3-bis(1-methylimidazol-2-yl)propionate.

Equilibrium	ΔH° kJ mol ⁻¹	ΔS° J K ⁻¹ mol ⁻¹
(1) $A^- + H^+ \rightleftharpoons AH$	-22.15	26.81
(2) $AH + H^+ \rightleftharpoons AH_2^+$	-14.43	13.88
(3) $AH_2^+ + H^+ \rightleftharpoons AH_3^{2+}$	-11.92	1.41
(4) $Fe^{2+} + A^- \rightleftharpoons FeA^+$	-7.28	39.96
(5) $FeA^+ + A^- \rightleftharpoons FeA_2$	-13.33	14.89

tend to be lipophilic rather than hydrophilic [23-27]. Studies in media other than water should provide some understanding of the chemistry of bio-ligands in living systems. The results given in Tables 5 and 6 show an increase in the pK_a value of the carboxylic group of 1-aminocyclopropane carboxylic acid with an increase of the concentration of dioxane (decreasing dielectric constant). An electrostatic model can explain the variation of pK_a for (OH) with solvent composition. In general, the stability of compounds containing an O-H link increases with increasing organic content of the solvent, due to the decrease in the dielectric constant of the bulk solvent. As the dielectric constant decreases, the ion-ion interaction involving the proton and the anionic oxygen donor of the ligand increases and consequently the pK_a increases.

Also, a careful examination of media effects on the pK_a of the NH₃⁺ group of 1-aminocyclopropane carboxylic acid and those of the protonated N-sites of 3,3-bis(1-methylimidazol-2-yl)propionic acid did not show a significant and systematic change with increasing dioxane content of the solvent. This can be explained by the non-electrostatic nature of the interaction between a neutral N-site and the positively charged hydrogen ion.

The results of medium effects on the formation constants of Fe^{2+} complexes with 1-aminocyclopropane carboxylic acid and 3,3-bis(1-methylimidazole-2-yl)propionic complexes are shown in Tables 5 and 6, and reveal an increase of the formation constants ($\log\beta_{110}$, $\log\beta_{120}$) upon addition of dioxane. This is explained on the premise that lowering the dielectric constant of the medium (by increasing the dioxane content) favours the interaction between the Fe^{2+} ion and the negatively charged 1-aminocyclopropane carboxylate anion and the 3,3-bis(1-methylimidazole-2-yl)propionate anion. As a result, the stability constant of the complexes increases.

3.4. Ternary complexes of Fe^{2+} with 3,3-bis(1-methylimidazol-2-yl)propionic acid and 1-aminocyclopropane carboxylic acid

Ternary complex formation may proceed either through a stepwise or simultaneous mechanism, depending on the formation constant of the Fe^{2+} complex with 3,3-bis(1-methylimidazol-2-yl)propionic acid and

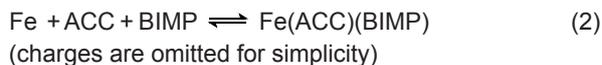
Table 5. Formation constants of Fe(II)-1-aminocyclopropane carboxylic acid complexes of general formula $Fe_p(ACC)_qH_r$ in dioxane-water solutions of different compositions at 25°C and 0.1 M NaNO₃.

System	Dioxane (%)	p	q	r ^a	Log β ^b	pK _a ^c
Fe-ACC	0	0	1	1	8.14(0.004)	8.14
		0	1	2	10.42(0.01)	2.28
		1	1	0	6.38(0.1)	
		1	2	0	10.72(0.1)	
Fe-ACC	12.5	0	1	1	8.39(0.009)	8.39
		0	1	2	11.90(0.01)	3.51
		1	1	0	7.49(0.03)	
		1	2	0	12.50(0.09)	
Fe-ACC	25	0	1	1	8.44 (0.05)	8.44
		0	1	2	12.18(0.08)	3.74
		1	1	0	7.62(0.04)	
		1	2	0	13.50(0.05)	
Fe-ACC	37.5	0	1	1	8.45(0.01)	8.45
		0	1	2	12.29(0.02)	3.84
		1	1	0	7.65(0.04)	
		1	2	0	14.50(0.05)	
Fe-ACC	50	0	1	1	8.46(0.01)	8.46
		0	1	2	12.65(0.01)	4.19
		1	1	0	7.90(0.01)	
		1	2	0	15.16(0.01)	
Fe-ACC	62.5	0	1	1	8.51(0.013)	8.51
		0	1	2	12.91(0.02)	4.40
		1	1	0	7.85(0.01)	
		1	2	0	14.98(0.02)	

Table 6. Formation constants of Fe(II)-BIMP complexes of general formula $Fe_p(BIMP)_qH_r$ in dioxane-water solutions of different compositions 25°C and 0.1 M NaNO₃.

System	Dioxane (%)	p	q	r ^a	Log β ^b	pK _a ^c
Fe- BIMP	0	0	1	1	7.11(0.01)	7.11
		0	1	2	11.31(0.02)	4.20
		0	1	3	13.50(0.03)	2.19
		1	1	0	6.07(0.05)	
Fe- BIMP	12.5	0	1	1	6.70(0.01)	6.70
		0	1	2	10.73(0.01)	4.03
		0	1	3	14.25(0.01)	3.52
		1	1	0	7.52(0.01)	
Fe- BIMP	25	0	1	1	6.69(0.01)	6.69
		0	1	2	10.73(0.02)	4.04
		0	1	3	14.24(0.02)	3.51
		1	1	0	7.71(0.01)	
Fe- BIMP	37.5	0	1	1	6.68(0.01)	6.68
		0	1	2	10.85(0.02)	4.17
		0	1	3	14.31(0.02)	3.46
		1	1	0	7.90(0.02)	
Fe- BIMP	50	0	1	1	6.66(0.01)	6.66
		0	1	2	10.98(0.02)	4.32
		0	1	3	14.42(0.02)	3.44
		1	1	0	8.02(0.02)	
Fe- BIMP	62.5	0	1	1	6.66(0.01)	6.66
		0	1	2	10.98(0.02)	4.32
		0	1	3	14.42(0.02)	3.44
		1	1	0	8.02(0.02)	
Fe- BIMP	62.5	0	1	1	6.93(0.01)	6.93
		0	1	2	11.72(0.01)	4.79
		0	1	3	14.91(0.01)	3.19
		1	1	0	10.37(0.02)	
Fe- BIMP	62.5	0	1	1	6.93(0.01)	6.93
		0	1	2	11.72(0.01)	4.79
		0	1	3	14.91(0.01)	3.19
		1	1	0	10.37(0.02)	
Fe- BIMP	62.5	0	1	1	6.93(0.01)	6.93
		0	1	2	11.72(0.01)	4.79
		0	1	3	14.91(0.01)	3.19
		1	1	0	10.37(0.02)	

1-aminocyclopropane carboxylic acid. The formation constant value of the Fe²⁺-3,3-bis(1-methylimidazol-2-yl)propionate complex (log K = 6.07) is of the same order as that of 1-aminocyclopropane carboxylic acid (log K = 6.36). It is reasonable to propose that in the presence of both ligands, the ternary complex is formed by the simultaneous mechanism, as given in Eq. 2, and the ternary complex is expressed by the general formula Fe(ACC)p(BIMP)q(H)r.



The potentiometric data of the ternary complex is best fitted assuming formation of the species with stoichiometric ratios of 1:1:1 (Fe : ACC : BIMP). The validity of this model was tested by comparing the experimental titration data with the theoretical simulated titration curve simulated used the formation constants of the complex formed. The experimental data coincides with the theoretical curve, Fig. 2, indicating the validity of the complex formation model.

The concentration distribution diagram of the ternary complex is shown in Fig. 3. The ternary complex starts to form at pH 4 and reaches the maximum concentration of 90% at pH 7.2. From the biological point of view, it is interesting to note that the ternary complex prevails in the physiological pH range and its formation is significant.

The enhancement of the stability of the ternary complexes can be investigated as follows:

(1) According to Sigel [27,28], the relative stability of the ternary complex Fe(BIMP)(ACC) compared to its binary complexes Fe(BIMP) and Fe(ACC) can be expressed quantitatively [27,29] by:

$$\Delta \log K = \log K_{Fe(BIMP)(ACC)}^{Fe} - (\log K_{Fe(BIMP)}^{Fe} + \log K_{Fe(ACC)}^{Fe}) \quad (3)$$

Fe(BIMP) (1:1) has fewer coordination sites than the solvated Fe²⁺ ion. Consequently, the secondary ligand (ACC) is expected to bind to the Fe(BIMP) complex with a smaller stability constant as compared to a Fe²⁺ ion. Therefore, Δlog K for any ternary complex is expected to be negative and generally have a value between -0.5 and -2.0 [27,29] depending on the geometry of the complex. The calculated Δlog K value (-0.39) is less negative than the theoretical value (-0.5). This may be considered as evidence for the occurrence of enhanced stabilities involving p-back donation from the negatively charged 1-aminocyclopropane carboxylate to the p-system of BIMP.

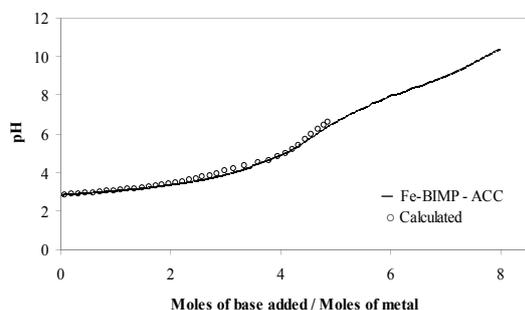


Figure 2. Potentiometric titration curve of Fe^{2+} -1-aminocyclopropane carboxylic acid -3,3-bis(1-methylimidazol-2-yl)propionic acid complexes at 25°C.

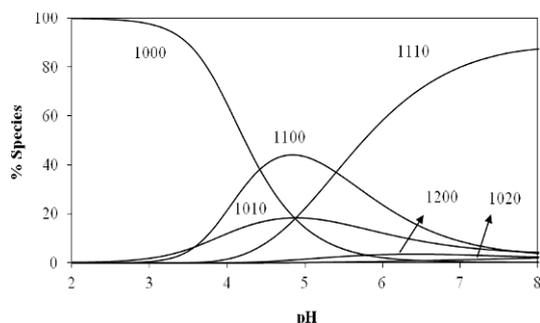


Figure 3. Concentration distribution diagram of Fe^{2+} -1-aminocyclopropane carboxylic acid -3,3-bis(1-methylimidazol-2-yl)propionic acid complexes at 25°C.

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(2) The quantitative stabilization of ternary complexes can be expressed in terms of their disproportionation constant X:

$$\text{Log } X = 2 \log \beta_{1110} - (\log \beta_{1200} + \log \beta_{1020}) \quad (4)$$

The value for log X expected from statistical arguments is +0.6 [27-30]. The values of log X for the Fe(BIMP)(ACC) ternary complex is 3.20 and higher than the statistical value (0.6), indicating marked stability of the ternary complex.

4. Conclusion

The plant hormone, ethylene, is biosynthesised from 1-aminocyclopropane carboxylic acid (ACC) using ACC oxidase (ACCO). ACCO is an iron(II) complex involving a nitrogenous ligand having imidazole and carboxylate groups as enzyme active sites. The interaction between ACC and ACCO leads to the formation of a mixed-ligand complex. Therefore, complex formation equilibria of ACC and 3,3-bis(1-methylimidazol-2-yl)propionic acid, especially those of mixed-ligand complexes with Fe^{2+} are highly relevant to the biological activity of this class of complexes.

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