

Equilibria in Aqueous Solutions of some Iron(II) Complexes

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Stepwise stability constants of complexes formed in the Fe^{2+} -oxalate(2-), -malonate(2-), -glycinate(1-), - β -alaninate(1-), -ethylenediamine, -diethylenetriamine, -triethylenetetra-amine, -iminodiacetate(2-), -nitrilotriacetate(3-), and ethylenediamine-*N,N'*-diacetate(2-) systems have been determined in aqueous solutions of 1 mol dm⁻³ KCl at 298 K using pH-metry. The equilibrium constants of the Fe^{2+} and Co^{2+} complexes are compared and similarities and differences in the co-ordination properties discussed.

Although the Fe^{2+} ion is a member of the first transition-metal series, studies on its equilibrium properties have been only rudimentary and literature data are rather uncertain (see Table 1). A discussion of the equilibrium data with regard to the co-ordination properties of Fe^{2+} complexes in aqueous solution has not so far been reported.

pH-Metric measurements have been carried out systematically herein by changing the number of oxygen and nitrogen donor atoms as well as the size of the ligands. Thus the Fe^{2+} -oxalate(2-) (ox), -malonate(2-) (mal), -glycinate(1-) (glyO), - β -alaninate(1-) (alaO), -ethylenediamine (en), -diethylenetriamine (dien), -triethylenetetra-amine (trien), -iminodiacetate(2-) (ida), -nitrilotriacetate(3-) (nta), and ethylenediamine-*N,N'*-diacetate(2-) (edda) systems were studied in order to augment the literature data. To interpret the results the co-ordination properties of Fe^{2+} and Co^{2+} were compared. This is permissible because of the similar chemical behaviour and size of the two ions (radii: Fe^{2+} , 76; Co^{2+} , 74 pm). The equilibrium properties of Co^{2+} complexes have been studied in detail.¹

The dynamics of equilibria in aqueous solutions of paramagnetic metal-ion complexes have previously been studied in this laboratory.^{2,3} To extend the studies to Fe^{2+} , the equilibrium data are required.

Experimental

The FeCl_2 stock solution was prepared by dissolving excess Fe powder in dilute HCl under an argon atmosphere. After the dissolution KOH was added until the precipitation of $\text{Fe}(\text{OH})_2$

(white!) and the solution was incubated for 1 d. After filtration the pH of the solution was adjusted to 3. This procedure gave an Fe^{3+} -free solution (checked by SCN^-).

The Fe^{2+} concentration was determined by titration with $\text{Ce}(\text{SO}_4)_2$ solution under an argon atmosphere and using ferroin [tris(1,10-phenanthroline)iron(II)] as an indicator. The acid concentration of the stock solution was determined pH-metrically using the appropriate Gran functions.⁴

The ligands en, dien, and trien were purified by vacuum distillation, the others by recrystallization from water. The protonation constants for all the ligands were checked.

The Radiometer PHM-52 pH-meter and GK-2310 B electrode used for pH measurements were calibrated for $-\log[\text{H}^+]$ at 298 K according to Irving *et al.*⁵ The ionic strengths of all the solutions were adjusted to 1 mol dm⁻³ KCl. The initial total concentrations used for pH titrations and the \bar{n} (average number of co-ordinated ligands) and pL ranges for complex formation are collected in Table 2. After evaluation of the formation curves the calculations were carried out with the program PSEQUAD.⁶

Results and Discussion

Evaluation of the formation curves showed that stepwise complex formation processes were dominant, disturbing hydrolysis appearing only in the higher pH range. In the final calculations parent complexes as well as hydroxo species were considered. The formation constants are given in Table 3.

The formation of $[\text{Fe}(\text{mal})]$, $[\text{Fe}(\text{alaO})]^+$, and $[\text{Fe}(\text{glyO})_3]^-$ were not detected in earlier works. The Fe^{2+} -edda system has

Table 1. Reported values for the formation constants of the Fe^{2+} -ligand (L) systems studied

Ligand	$\log \beta_{\text{FeL}}$	$\log \beta_{\text{FeL}_2}$	$\log \beta_{\text{FeL}_3}$	Medium (I/mol dm ⁻³)	T/K	Ref.
ox	3.05	5.15		NaClO_4 (1)	298	a
mal		2.22		NaClO_4 (0.5)	298	b
glyO	4.13	7.65		KNO_3 (0.1)	298	c
alaO		~4		H_2O (0.01)	293	d
en	4.34	7.65	9.70	KCl-HCl (1.4)	298	e
dien	6.23	10.36		KCl-KNO ₃ (1)	303	f
trien	7.8			KCl (0.1)	293	g
ida	5.54	9.81		NaClO_4 (0.5)	298	h
nta	8.83	12.8 ⁱ		KCl (0.1)	293	j

^a E. Bottari and L. Ciavatta, *Gazz. Chim. Ital.*, 1965, **95**, 908. ^b W. B. Schaap, H. A. Laitinen, and J. C. Bailar, *J. Am. Chem. Soc.*, 1954, **76**, 5868. ^c A. Gergely, *Acta Chim. Acad. Sci. Hung.*, 1969, **59**, 309. ^d A. Albert, *Biochem. J.*, 1950, **47**, 531. ^e R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, 1957, **11**, 1419. ^f H. J. Jonassen, *J. Phys. Chem.*, 1952, **56**, 16. ^g G. Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 974. ^h A. Napoli, *J. Inorg. Nucl. Chem.*, 1972, **34**, 987. ⁱ See ref. 1. ^j G. Schwarzenbach, G. Anderegg, W. Scheider, and H. Senn, *Helv. Chim. Acta*, 1955, **38** 1147.

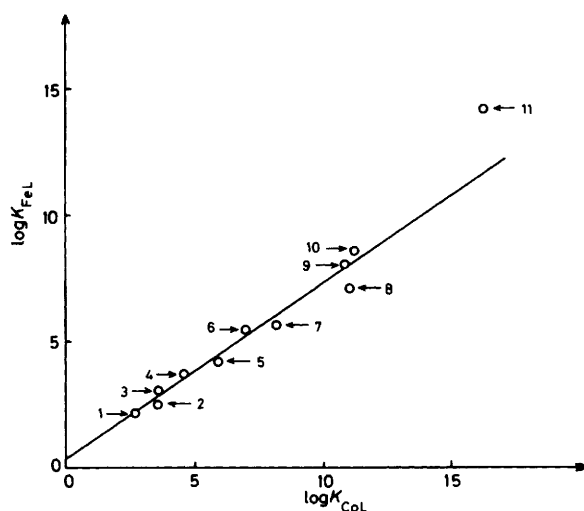
Table 2. Initial total concentrations of ($T^0/\text{mol dm}^{-3}$) solutions used for pH-metric titrations and the \bar{n} and pL ranges studied

Ligand	T_H^0	T_L^0	T_M^0	\bar{n} range	pL range	Ligand	T_H^0	T_L^0	T_M^0	\bar{n} range	pL range
ox	0.040 66	0.040 00	0.006 87	0.2—1.8	3.3—1.8	dien	0.077 42	0.026 96	0.011 46	0.1—1.9	7.3—3.0
	0.040 84	0.040 00	0.013 74				0.092 96	0.032 36	0.010 30		
	0.040 75	0.040 00	0.003 43				0.108 50	0.037 75	0.013 74		
	0.040 57	0.040 00	0.010 30				0.154 94	0.053 93	0.017 17		
mal	0.041 01	0.040 00	0.017 28	0.1—1.2	3.5—1.9	trien	0.082 02	0.020 00	0.013 74	0.1—1.0	8.0—5.6
	0.040 66	0.040 00	0.010 62				0.083 18	0.020 00	0.009 54		
	0.056 85	0.056 00	0.025 71				0.053 19	0.015 00	0.006 28		
	0.056 67	0.056 00	0.021 35				0.064 19	0.015 00	0.014 53		
glyO	0.201 07	0.200 00	0.010 09	0.1—2.6	4.6—2.0	ida	0.080 36	0.040 00	0.013 74	0.1—2.0	6.4—2.5
	0.200 68	0.200 00	0.007 01				0.080 45	0.040 00	0.017 17		
	0.100 47	0.000 00	0.008 97				0.040 41	0.020 00	0.007 85		
	0.400 72	0.400 00	0.013 54				0.040 37	0.020 00	0.009 97		
alaO	0.208 33	0.204 15	0.010 51	0.1—1.1	4.4—1.8	nta	0.025 59	0.020 00	0.006 87	0.3—1.8	8.4—2.8
	0.104 17	0.102 19	0.007 02				0.051 10	0.040 00	0.010 30		
	0.400 34	0.400 00	0.015 38				0.051 19	0.040 00	0.013 74		
	0.400 24	0.400 00	0.008 36				0.051 28	0.040 00	0.017 17		
en	0.072 91	0.033 44	0.007 68	0.1—2.6	5.5—2.2	edda	0.098 89	0.030 00	0.010 30	0.1—1.3	9.5—2.3
	0.145 81	0.066 88	0.007 68				0.049 35	0.018 00	0.006 87		
	0.149 37	0.066 88	0.013 74				0.069 26	0.021 00	0.085 85		
	0.148 48	0.066 88	0.010 30				0.197 87	0.060 00	0.024 04		

Table 3. Stability constants of the Fe^{2+} complexes, formation constants of Co^{2+} mono complexes, and $\Delta \log K_{\text{CoFe}}$ values

Ligand	$\log \beta_{\text{FeL}}$	$\log \beta_{\text{FeL}_2}$	$\log \beta_{\text{FeL}_3}$	$\log \beta_{\text{CoL}}^*$	$\Delta \log K_{\text{CoFe}}$
ox	3.05 ± 0.02	5.01 ± 0.02		3.25	0.20
mal	2.24 ± 0.01			2.97	0.73
glyO	3.73 ± 0.01	6.65 ± 0.01	8.87 ± 0.01	4.57	0.84
alaO	2.53 ± 0.01			3.58	1.05
en	4.26 ± 0.01	7.73 ± 0.01	10.17 ± 0.02	5.96	1.70
dien	5.66 ± 0.02	9.61 ± 0.02		8.00	2.34
trien	7.12 ± 0.03			11.35	4.23
ida	5.45 ± 0.03	9.82 ± 0.03		6.94	1.49
nta	8.05 ± 0.01	11.53 ± 0.03		10.38	2.33
edda	8.63 ± 0.01	10.67 ± 0.03		11.25	2.62

* Data from ref. 1.

**Figure.** Correlation between the stability constants of Fe^{2+} and Co^{2+} mono complexes with $\text{L} = \text{mal}$ (1), alaO (2), ox (3), glyO (4), en (5), ida (6), dien (7), trien (8), nta (9), edda (10), or ethylenediaminetetra-acetate (4—) (ref. 1) (11)

not been previously studied. For the Fe^{2+} -mal and -alaO systems, formation constants are given for the mono complexes only (in the case of the bis complexes $\log K_2 < 2$ was calculated but these values are rather uncertain).

The fundamental co-ordination properties of Fe^{2+} and Co^{2+} are similar as shown in the Figure. Values of $\Delta \log K_{\text{CoFe}} = \log K_{\text{Co}} - \log K_{\text{Fe}}$ (see Table 3) indicate a greater degree of covalent bonding in the Co^{2+} complexes as a consequence of the different electron structures.

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References

- 1 A. E. Martell and R. M. Smith, 'Critical Stability Constants,' Plenum Press, New York and London, 1974–1977, vols. 1–4; 1982, vol. 5.
- 2 I. Nagypál, F. Debreczeni, and R. E. Connick, *Inorg. Chim. Acta*, 1981, **48**, 225.

- 3 I. Nagypál, K. Micskei, and F. Debreczeni, *Inorg. Chim. Acta*, 1983, **77**, L161.
4 G. Gran, *Acta Chem. Scand.*, 1950, **4**, 559.
5 H. Irving, M. G. Miles, and L. D. Pettit, *Anal. Chim. Acta*, 1967, **38**, 475.

- 6 L. Zékány and I. Nagypál, in 'Computational Methods for the Determination of Formation Constants,' ed. D. J. Leggett, Plenum Press, New York, 1985, p. 291.

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