# Metal–Metal Bond Equilibria in Aqueous Solution. II. Zinc Hydroxotetracarbonylferrates(–II)*

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*The reaction of tetracarbonylferrate(–II) anion with* $Zn^{2+}$ *was studied potentiometrically in the neutral and alkaline ranges of pH. On the basis of equilibrium measurements of hydrogen ion concentrations at 20° C and a total normality of 1.0 (NaClO₄), the existence of a number of species is indicated, including polynuclear mixed hydroxocomplexes. The constant* $K_2 = 1.1 \times 10^5$ $M^{-1}$ *is obtained for the equilibrium* $ZnFe(CO)_4 +$ $Fe(CO)_4{}^{2-} \rightleftarrows [ZnFe(CO)_4]_2{}^{2-}$. *The existence of other species is indicated:*
$Zn_4[Fe(CO)_4]_4 \ (OH)_4{}^{4-}$, $Zn_2Fe(CO)_4(OH)_3{}^-$, $Zn_4$ $[Fe(CO)_4]_3(OH)_3{}^-$ *and* $Zn_2Fe(CO)_4(OH)_2$. *This strong tendency to the formation of mixed hydroxocomplexes is explained by the ability of the tetracarbonylferrate anion to keep zinc dissolved at pH's above neutrality, without occupying all of its co-ordinating sites.*

## Introduction

Zinc derivatives of iron tetracarbonylhydride have been unknown until very recently[1]. In a previous paper[2], we have reported on their existence in aqueous solutions and we have shown that a number of species $(ZnFe(CO)_4, ZnHFe(CO)_4{}^+, Zn_2Fe(CO)_4{}^{2+})$ participate in the equilibria involving $Zn^{2+}$ and $Fe(CO)_4{}^{2-}$ ions.

These complexes differ from the mercury[3], cadmium[4] and other heavy-metal derivatives known[5], which are insoluble and very likely polymeric[6] species. A particular reason for their interest is that they are among the first and few examples of compounds having dissociable metal–metal bonds, in aqueous solution[7].

The anion $Fe(CO)_4{}^{2-}$ was shown to be a very strong co-ordinating agent and the stability constant which was found for the zinc complex, $ZnFe(CO)_4$, was orders of magnitude higher than the figures obtained for most zinc complexes of monodentate ligands[8].

This paper presents further potentiometric data on this system. This data refers to a range of pH and ligand concentration which was not examined previously. Its detailed analysis was done by different methods, including a least-squares procedure for data reduction and computation of stability constants.

## Experimental

A detailed description of the experimental procedures used is in a previous paper[2]. It is necessary to give the reasons for the rather odd experimental design. The hydride, $H_2Fe(CO)_4$, is very unstable which prevents the usual titrations of metal ion plus ligand with hydroxide. These limitations of experimental design also limit the methods of calculation which may be used.

Another experimental limitation was the unsuitability of zinc-reversible amalgam electrodes, due to the very low free zinc ion concentration and to the possibility of interaction between mercury and the iron carbonyl derivatives.

To make the analysis of the experimental data possible, a nonlinear least-squares multiple regression method was used to set up a computer program. This program[15] is analogous to others published[9] and has been used on an IBM 360/44 computer.

## Results

Table I gives the experimental data from the potentiometric titrations of $Fe(CO)_4{}^{2-} + HFe(CO)_4{}^-$ with zinc perchlorate. Figures 1 and 2 show some of the titration curves. Each point given is the average of at least three, up to eight independent experiments.

All the titration curves present two inflexion points, corresponding to species of metal: ligand stoichiometry equal to 1:1 and 1:2. As we have pointed out previously[2] the ligand may be either OH⁻ or $Fe(CO)_4{}^{2-}$, or both. Consequently, species like $Zn[Fe(CO)_4]_2{}^{2-}$ and $Zn_4[Fe(CO)_4]_4(OH)_4{}^{4-}$ are called here 1:2 complexes. The curves have three major regions, indicated in figure 1. Region 3, before the first inflexion point, is the least interesting and its analysis is very complicated due to the existence of hydroxocomplexes of zinc.

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* Paper I in this series is ref. 2.

TABLE I (a). Titration Data.[a]

| Titration | C | D | E | F | G | H | I | K |
|---|---|---|---|---|---|---|---|---|
| Initial $C_{OH}$ ($M$) × $10^2$ | 0.5077 | 0.5077 | 0.5077 | 0.5077 | 0.5077 | 2.017 | 2.026 | 2.026 |
| Initial $C_{HL}$ ($M$) × $10^2$ | 2.467 | 1.493 | 0.990 | 0.685 | 0.586 | 4.000 | 2.961 | 2.469 |
| Molarity of Zinc Solution × $10^2$ | 0.633 | 0.633 | 0.633 | 0.633 | 0.633 | 2.532 | 2.532 | 2.532 |

| $v_{Zn}$ | pH | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 0 | 11.512 | 11.592 | 11.562 | 11.620 | 11.626 | 12.068 | 12.110 | 12.134 |
| 1 | 11.177 | 11.247 | 11.220 | 11.268 | 11.272 | 11.700 | 11.747 | 11.765 |
| 1.6 | 10.758 | 10.816 | 10.792 | 10.831 | 10.835 | 11.188 | 11.234 | 11.254 |
| 1.7 | – | – | – | – | – | 11.025 | – | – |
| 1.75 | 10.562 | 10.620 | 10.600 | 10.636 | 10.639 | 10.925 | 10.985 | 11.001 |
| 1.8 | – | – | – | – | – | 10.820 | – | – |
| 1.85 | 10.385 | 10.442 | 10.420 | 10.461 | 10.467 | 10.660 | 10.734 | 10.746 |
| 1.9 | 10.248 | 10.333 | 10.314 | 10.356 | 10.369 | 10.475 | 10.557 | 10.572 |
| 1.95 | 10.132 | 10.222 | 10.198 | 10.245 | 10.265 | 10.220 | 10.324 | 10.345 |
| 2.0 | 10.110 | 10.102 | 10.078 | 10.130 | 10.165 | 9.945 | 10.052 | 10.075 |
| 2.05 | 9.897 | 9.990 | 9.963 | 10.019 | 10.064 | 9.707 | 9.806 | 9.832 |
| 2.1 | 9.792 | 9.880 | 9.854 | 9.917 | 9.960 | 9.534 | 9.618 | 9.651 |
| 2.2 | 9.610 | 9.696 | 9.669 | 9.734 | 9.758 | 9.300 | 9.373 | 9.412 |
| 2.3 | 9.465 | 9.550 | 9.521 | 9.575 | 9.576 | 9.144 | 9.211 | 9.246 |
| 2.4 | 9.346 | 9.430 | 9.400 | 9.435 | 9.420 | 9.029 | 9.087 | 9.115 |
| 2.6 | 9.159 | 9.240 | 9.214 | 9.214 | 9.183 | 8.851 | 8.896 | 8.914 |
| 2.8 | 9.008 | 9.085 | 9.063 | 9.046 | 9.009 | 8.709 | 8.743 | 8.745 |
| 3.0 | 8.872 | 8.951 | 8.931 | 8.902 | 8.860 | 8.578 | 8.598 | 8.588 |
| 3.2 | 8.735 | 8.816 | 8.801 | 8.764 | 8.719 | 8.449 | 8.457 | 8.438 |
| 3.4 | 8.578 | 8.675 | 8.663 | 8.617 | 8.570 | 8.310 | 8.313 | 8.284 |
| 3.6 | 8.382 | 8.506 | 8.494 | 8.450 | 8.405 | 8.146 | 8.150 | 8.117 |
| 3.7 | 8.263 | 8.407 | 8.387 | 8.357 | 8.320 | 8.040 | 8.055 | 8.027 |
| 3.8 | 8.108 | 8.291 | 8.248 | 8.254 | 8.225 | 7.908 | 7.944 | 7.915 |
| 3.9 | 7.920 | 8.154 | 8.073 | 8.144 | 8.135 | 7.713 | 7.798 | 7.787 |
| 4.0 | 7.688 | 7.975 | 7.861 | 8.030 | 8.042 | 7.462 | 7.603 | 7.630 |
| 4.1 | 7.450 | 7.790 | 7.644 | 7.915 | 7.955 | 7.218 | 7.383 | 7.450 |
| 4.2 | 7.252 | 7.630 | 7.450 | 7.800 | 7.870 | 7.037 | 7.202 | 7.293 |
| 4.4 | 6.983 | 7.388 | 7.183 | 7.610 | 7.718 | 6.795 | 6.958 | 7.060 |
| 4.8 | 6.701 | 7.098 | 6.894 | 7.358 | 7.500 | 6.516 | 6.675 | 6.797 |
| 5.5 | 6.422 | – | 6.616 | 7.107 | 7.258 | 6.257 | 6.423 | 6.547 |
| 6.0 | – | 6.848 | – | – | – | – | – | – |
| 6.5 | 6.209 | 6.627 | 6.406 | 6.905 | 7.065 | 6.044 | 6.210 | 6.344 |
| 8.0 | 6.015 | 6.442 | 6.210 | 6.723 | 6.887 | 5.850 | 6.025 | 6.164 |

[a] Initial volume: 50.0 ml in all experiments

Regions 1 (beyond the second inflexion point) and 2 (between the two inflexions) are discussed below. The lack of regularities in the different titration curves indicates the complexity of the system.

*Region 1*

The experimental situation in the region 1 of the titration curves has some similarities to the former data from titrations of $HFe(CO)_4^-$ only with $Zn^{2+}$. In both cases the pH region is similar, there is an appreciable concentration of free $Zn^{2+}$ ions and only species with a metal : ligand ratio equal to or greater than one are possibly important. Also, protonated species are expected to occur and hydroxocomplexes are not likely to dominate. On the other hand, the two sets of data differ in the total concentration of zinc, which is much higher in the present data. A larger proportion of the added zinc should now be found in complexed form. The present situation may be formally represented as a titration of $ZnFe(CO)_4$ plus $HFe(CO)_4^-$ with zinc ions.

Consequently, the same set of species (and constants) previously obtained should apply here. However, no good fit is obtained unless a polynuclear complex is also introduced. The best of the many possibilities considered: $Zn_2Fe(CO)_4(OH)^+$, $Zn_2[Fe(CO)_4]_2$, $Zn_3[Fe(CO)_4]_2(OH)^+$, $Zn_3Fe(CO)_4(OH)_2^{2+}$ and their combinations, is the third species. The equilibrium constant,

TABLE I (b). Titration Data.[a]

| Titration | A | B | J |
|---|---|---|---|
| Initial $C_{OH}$ ($M$) × $10^2$ | 1.008 | 0.2538 | 0.2538 |
| Initial $C_{HL}$ ($M$) × $10^2$ | 2.995 | 2.205 | 4.976 |
| Molarity of Zinc Solution × $10^2$ | 2.532 | 0.633 | 0.633 |

| $v_{Zn}$ | pH | | |
|---|---|---|---|
| 0 | 11.790 | 11.210 | 11.333 |
| 0.5 | 11.436 | 10.900 | 11.005 |
| 0.8 | 10.973 | 10.514 | 10.612 |
| 0.875 | 10.745 | 10.346 | 10.449 |
| 0.925 | 10.513 | 10.210 | 10.320 |
| 0.95 | 10.350 | 10.135 | 10.248 |
| 0.975 | 10.160 | 10.056 | 10.173 |
| 1.0 | 9.980 | 9.981 | 10.096 |
| 1.025 | 9.813 | 9.902 | 10.020 |
| 1.05 | 9.667 | 9.824 | 9.948 |
| 1.1 | 9.455 | 9.680 | 9.812 |
| 1.15 | 9.300 | 9.554 | 9.688 |
| 1.2 | 9.180 | 9.443 | 9.583 |
| 1.3 | 9.000 | 9.256 | 9.396 |
| 1.4 | 8.855 | 9.094 | – |
| 1.5 | 8.725 | 8.944 | 9.088 |
| 1.6 | 8.597 | 8.788 | 8.955 |
| 1.7 | 8.457 | 8.618 | 8.807 |
| 1.8 | 8.280 | 8.410 | 8.636 |
| 1.85 | 8.160 | 8.280 | 8.539 |
| 1.9 | 8.003 | 8.125 | 8.430 |
| 1.95 | 7.79 | 7.947 | 8.305 |
| 2.0 | 7.54 | 7.738 | 8.162 |
| 2.05 | 7.295 | 7.508 | 8.005 |
| 2.1 | 7.122 | 7.305 | 7.880 |
| 2.2 | 6.880 | 7.040 | 7.670 |
| 2.4 | 6.605 | 6.732 | 7.392 |
| 2.75 | 6.342 | 6.457 | 7.128 |
| 3.25 | 6.124 | 6.233 | 6.923 |
| 4.0 | 5.928 | 6.042 | 6.725 |
| 5.0 | 5.758 | – | – |

[a] Initial volume: 50.0 ml in all experiments.

$$K = \frac{<Zn_3[Fe(CO)_4]_2OH> <HFe(CO)_4>}{<ZnFe(CO)_4>^3} = 29 \pm 3$$

was obtained from a simultaneous fit with the constants formerly obtained for the species $Zn_2Fe(CO)_4^{2+}$, $ZnFe(CO)_4$, $ZnHFe(CO)_4^+$, $H_2Fe(CO)_4$ using a set of 45 experimental points, where each one was the average of at least three experimental determinations. Also, this calculation confirmed the constants previously obtained.

*Region 2*

The analysis of the experimental data from region 2 was done by graphical and least-squares procedures. The preliminary analysis of the data showed that:
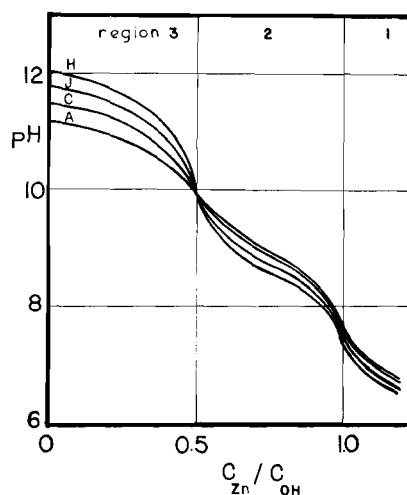


Figure 1. Potentiometric titrations of solutions containing $Na_2Fe(CO)_4$ and $NaHFe(CO)_4$ with zinc perchlorate. The pertinent data are in Table I.
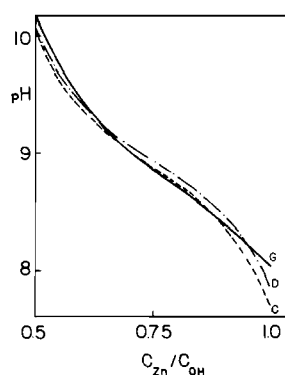


Figure 2. Potentiometric titrations of solutions containing $Na_2Fe(CO)_4$ and $NaHFe(CO)_4$ with zinc perchlorate. See Table I.

a) no simple pattern of complex formation is observed; plots like those used by Martell[10] did not fit many points;

b) on the average, the 1:2 species are polynuclear complexes of a higher degree than the 1:1 species. In our previous paper, assuming the complex $ZnFe(CO)_4$ to be the only 1:1 species, the 1:2 species were reported to be predominantly dimers. Since the trinuclear complex, $Zn_3[Fe(CO)_4]_2OH$, is now shown to be present in appreciable concentrations, higher polynuclear 1:2 species have to be considered;

c) the 1:2 species include mixed hydroxocomplexes; the existence of these complexes was already suggested, in an early stage of this work, by the observation of a high solubility of $Zn(OH)_2$ in zinc carbonylferrate solutions;
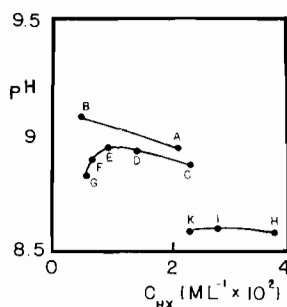
Figure 3. Plots of pH vs. $C_{HFe(CO)_4}$ at $C_{Zn}/C_{OH} = 0.75$. The lines drawn link points of identical $C_{Zn}$ and $C_{OH}$. The observed upward trend at low $C_{HFe(CO)_4}$ and high $C_{Zn}$ and $C_{OH}$ requires the existence of species whose stoichiometry is not $1:1$ or $1:2$.

d) the effect of a variation of $C_{HFe(CO)_4-}$ on theoretical titration curves including only $1:2$ and $1:1$ complexes is such that plots of pH vs. $C_{HFe(CO)_4-}$ at fixed $C_{Zn}$ and $C_{OH}$ are monotonic curves of negative slope. This is not the case in the present system. The only way to have the trends observed (Figure 3) is to have species of an intermediate stoichiometry ($2:3$, $3:4$, *etc.*);

e) Some very likely species, such as $ZnFe(CO)_4OH^-$, $Zn_2[Fe(CO)_4]_2(OH)_2^{2-}$ were systematically rejected in the least-squares analysis. Also, the fit of the data in

TABLE II. Equilibrium Constants.

| Species | Equilibrium Constants[a] | Sum of Squares of $C_1$ Residuals[b] |
|---|---|---|
| $Zn_4[Fe(CO)_4]_4(OH)_4^{4-}$ | $0.958 \times 10^{-29}$ | |
| $Zn[Fe(CO)_4]_2^{2-}$ | $0.229 \times 10^{-7}$ | |
| $Zn_2Fe(CO)_4(OH)_3^-$ | $0.318 \times 10^{-18}$ | $0.80 \times 10^{-6}$ |
| $Zn_4[Fe(CO)_4]_3(OH)_3^-$ | $0.751 \times 10^{-13}$ | |
| $Zn_2Fe(CO)_4(OH)_2$ | $0.120 \times 10^{-9}$ | |
| | | |
| $Zn_4[Fe(CO)_4]_4(OH)_4^{4-}$ | $0.88 \times 10^{-29}$ | |
| $Zn[Fe(CO)_4]_2^{2-}$ | $0.23 \times 10^{-7}$ | |
| $Zn_2Fe(CO)_4(OH)_3^-$ | $0.36 \times 10^{-18}$ | $0.88 \times 10^{-6}$ |
| $Zn_4[Fe(CO)_4]_3(OH)_3^-$ | $0.85 \times 10^{-13}$ | |
| | | |
| $Zn_4[Fe(CO)_4]_3(OH)_5^{3-}$ | $0.54 \times 10^{-13}$ | |
| $Zn[Fe(CO)_4]_2^{2-}$ | $0.27 \times 10^{-7}$ | |
| $Zn_2Fe(CO)_4(OH)_2$ | $0.46 \times 10^{-9}$ | $0.12 \times 10^{-5}$ |
| $Zn_4[Fe(CO)_4]_3(OH)_3^-$ | $0.54 \times 10^{-13}$ | |
| | | |
| $Zn_3[Fe(CO)_4]_3(OH)_3^-$ | $0.37 \times 10^{-22}$ | |
| $Zn[Fe(CO)_4]_2^{2-}$ | $0.19 \times 10^{-7}$ | |
| $Zn_2Fe(CO)_4(OH)_3^-$ | $0.21 \times 10^{-18}$ | $0.12 \times 10^{-5}$ |
| $Zn_2Fe(CO)_4(CO)_2$ | $0.21 \times 10^{-9}$ | |
| $Zn_4[Fe(CO)_4]_3(OH)_3^-$ | $0.63 \times 10^{-13}$ | |

[a] Formation constants from $H^+$, $HFe(CO)_4^-$, $ZnFe(CO)_4$.
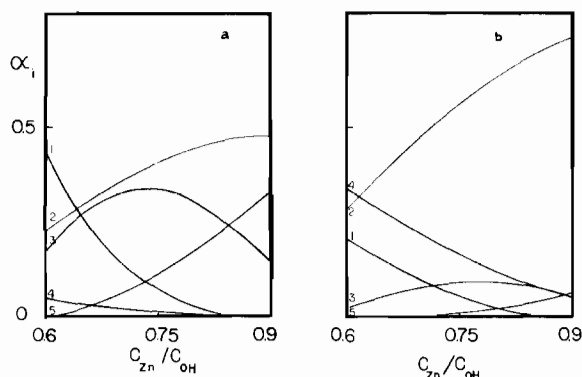[b] For 70 independent experimental points, each one being the average of 3 to 8 measurements.



Figure 4. Relative amounts of zinc present as any of the major complex species: 4a, titration K; 4b, titration B. Curves 1, $Zn_4[Fe(CO)_4]_4(OH)_4^{4-}$; 2, $ZnFe(CO)_4$; 3, $Zn_4[Fe(CO)_4]_3$ $(OH)_3^-$; 4, $Zn_2Fe(CO)_4(OH)_3^-$; 5, $Zn_3[Fe(CO)_4]_2OH^+$.

this analysis was improved by the introduction of complexes of formulae $Zn_3[Fe(CO)_4]_a(OH)_{6-a}$ and $Zn_4[Fe (CO)_4]_b(OH)_{6-b}$ but it became worse when $Zn_5[Fe (CO)_4]_c(OH)_{10-c}$ and bigger species were tried.

A number of sets of species was thus submitted to the least-squares analysis. The best among those are in Table II which gives the formulae of the species, the final refined equilibrium constants and the weighted summations of the residuals. The best set includes three $1:2$ and two $2:3$ species. Any set which gave a reasonable fit includes at least the following: $Zn[Fe(CO)_4]_2$, another $1:2$ and a $2:3$ species, both mixed hydroxo polynuclear complexes. The relative importance of different species at different sets of analytical concentrations varies considerably, as shown in Figure 4 (curves calculated using the best set of constants).

Both sets which gave the best fit can be used to calculate the pH's of the solutions, within $\pm$ 0.03 of the experimental pH's, slightly above the experimental reproducibility of measurements.

**Discussion**

Long ago, Sillén[11] pointed out that strong ligands capable to keep metal ions in solution at high pH are necessary to originate mixed hydroxocomplexes, if the ligands do not occupy all the binding sites of the metal ion. These conditions are perfectly fulfilled by the ligand tetracarbonylferrate(–II) and this is the reason for the complexity of this system and for the difficulty found in its analysis. In another case which was worked out in this laboratory (G.H.M. Dias, personal communication), cadmium was shown to be complexed by the carbonylferrate anion but mixed hydroxocomplexes were unimportant, as usually happens with zinc.

Mixed hydroxocomplexes have not been studied frequently and most of the reported work was done on

a narrow range of concentrations. This is quite misleading, as we found many times in this work. It is always possible to fit limited sets of data to species which are not supported when the whole body of data is considered.

On the other side, measurements on a wide range of concentrations suffer of many disadvantages, related to the possibility of variations of the activity coefficients and of the junction potentials of the measuring cell[12]. In our case, those problems were minimised by making $NaClO_4$ to be 95% or more of the total ionic concentration. It has also been suggested[13] that high ionic strengths might induce the formation of polynuclear species. However, it is possible that polynuclear species are seen more frequently at high ionic strengths just because the higher metal and ligand concentrations used lead to their formation. Unhappily, the description of these systems still has to rest largely on very indirect approaches, such as those used in this study. Some degree of indefinition in the description of the system is left but it was certainly possible to attain a clear picture of a quite untractable system.

The large number of species which were revealed in this study is easily understood: tetracarbonylferrate ion is a non-chelating, bidentate ligand and $Zn^{2+}$ is a cation prone to hydroxo complex formation. Since hydroxocomplexes tend to be polynuclear species, we ended up with a situation very complex indeed.

The most interesting number among all the equilibrium constants calculated in this study is the constant for the formation of the complex $Zn[Fe(CO)_4]_2^{2-}$, $K_2 = 1.1 \times 10^5 M^{-1}$. It is certainly much less than $K_1 = 4 \times 10^8$ $M^{-1}$ but it is comparable to $K_1$ of zinc complexes of good ligands such as cyanide or aminoacetate[8].

It should be pointed out that this kind of situation is probably the rule, when one deals with complexes of certain metal ions in alkaline or neutral medium. It is rather curious that in metal–protein complexes, in which the participation of small anions may be very important[14], OH⁻ is not usually considered as a prospective participant in the complex formation.

## Acknowledgments

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