

Incorporation of Organic Complexing Agents in Electromotive Force-pH Diagrams[☆]

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ABSTRACT

One of the limitations to using thermodynamic electromotive force (EMF)- or potential-pH diagrams is the inability to include organic ions and the products of their interaction with metals in the data base. Formation of such products may affect corrosion. This paper provides a method for deriving the free energies of formation of such species in the standard state of 1 molal (m) concentration, unit activity coefficient, 298 K. The methodology is used to derive the thermodynamic EMF-pH diagram for iron in the presence of iminodiacetic acid, a compound known to form dissolved complexes with iron.

INTRODUCTION

Thermodynamic electromotive force (EMF)-pH diagrams, as originally developed by Pourbaix,¹ have been shown to be practical tools for corrosion prediction. The EMF (potential) and pH coordinates in which these diagrams are plotted are useful to the corrosion engineer because pH, a measure of acidity, and EMF (potential), a measure of oxidizing power, are important determinants of corrosion in electrolyte solutions. The species shown on the diagram are the most thermodynamically stable. They have the minimum free energy at each (pH, EMF) coordinate for the conditions used to calculate the diagram. If all components important to corrosion of the metal in the particular environment are included in a particular diagram, the diagram can serve as a corrosion *road map*. The diagram can show under which pH and potential conditions corrosion does not occur. Immunity or pure metal is the most stable state under these conditions. The diagrams show which pH and potential conditions *might* cause transformation of a metal to an ion (metal loss) or oxidized solid (possible passivity). The important point is that since the diagrams are thermodynamic, they only show what reaction might occur in the real system. Kinetic experiments (e.g., coupon immersion tests, polarization scans, electrochemical impedance measurements) are required to show what does occur under the actual system conditions.

As discussed previously,² two uses of the diagrams have emerged. The first use is as an aid in data interpretation³⁻⁵ after the complex kinetic experiments have been completed. The second use is in conjunction with simple pH and corrosion potential measurements to predict the possibility of corrosion before the complex kinetic tests are performed.^{2,6} This usage is the classical

application of thermodynamics to determine if and what type of kinetic experiments are needed.

However, both uses are limited by the data base from which the diagrams are constructed. Numerous deficiencies exist in the present data base, even for simple diagrams with no organic species.⁷⁻⁹ More importantly, most thermodynamic data for components in aqueous solutions are for inorganic compounds and ions¹⁰⁻¹² and simple organic compounds.¹¹ However, many corrosive systems contain larger organic species which may interact with the metal possibly forming ionic complexes between the metal and organic components. Such formation may initiate or accelerate corrosion. Thus, the practical application of these diagrams has been somewhat limited by the inability to include larger organic ions and the products of their interaction with metals directly on the diagrams. An example of such a need was pointed out recently in an example in which a cadmium-ethylene diamine tetraacetic acid (EDTA) complex drastically changed the cadmium-water EMF-pH diagram in a way consistent with experimental observation.¹³ The diagram was consistent with the increased dissolution observed when EDTA was present. The diagram supported the idea that EDTA could accelerate cadmium corrosion under the pH and potential conditions in the process.

To place an organic compound on the thermodynamic EMF-pH diagram, the thermodynamic properties must be known at the standard state of the solution. Such properties must be estimated when tabulations do not exist. Since thermodynamic functions are state functions independent of path, the estimation can, in principle, be done by creating an artificial path from the elements to the final product. This path is chosen so that it passes through states for which thermodynamic functions are known or can be estimated. A method was introduced previously¹³ in which the path was created to pass through states for which thermodynamic properties can be estimated. In some of those states, the compound would not exist naturally; such states are called *virtual states*.

The purpose of this paper is to present a more formalized procedure for making these estimates than that used previously.¹³ The steps in this procedure use group contribution estimation techniques for thermodynamic properties of a dissolved organic species. An actual example is used to demonstrate that a diagram generated by this method is consistent with observed corrosion behavior. Unfortunately, few experimental results are available to confirm that a complex ion predicted to exist at a given pH and potential does, indeed, exist there. Hence, direct experimental confirmation of the compounds predicted by the procedure is usually unavailable in the literature.

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ESTIMATION PROCEDURE

Thermodynamic properties such as free energy, entropy, and enthalpy are functions of the state of the compound and are independent of how the compound is formed.¹⁴ For example, the free energy of formation of liquid water at 298 K, 1 atmosphere (atm) pressure, is the same whether the water is formed directly from gaseous hydrogen and oxygen or from ice. Path independence is the property that enables organic ions in aqueous solutions to be placed on the potential-pH diagrams.

Construction of an appropriate path by which the molecule is formed from the elements must be done carefully. The path must end at the state of 1 molal (m) concentration, zero ionic strength (ideal solution). The intermediate states must be those that allow for estimation of intermediate thermodynamic properties. As for the organic molecules, both tabulations for small molecules¹⁵ and estimation methods by group contribution for large complex molecules¹⁶ exist for organic molecules in the vapor state, 1 atm pressure, 298 K. Therefore, the first step is to form the molecule as a pure component at 298 K, 1 atm pressure in the vapor state. Since large organic molecules, as considered here, usually do not exist naturally under these conditions, this state is often a virtual state.

The next step is to take the molecule from this vapor state into water in the un-ionized state at 1 m concentration and zero ionic strength unit activity coefficient. This portion of the path is the most difficult because experimental data required often do not exist. However, recent attempts to exploit the group contribution theory have begun to overcome this problem. The procedure is to estimate the free energy and enthalpy change when moving from the vapor state to 1 m concentration in an ideal aqueous solution by adding the contributions from each major group in the molecule.¹⁷ Though not all groups are represented, the data do enable properties to be estimated for a number of compounds of significance in corrosion studies. Finally, measured pK values and stability constants are used to estimate thermodynamic properties of the ionic forms of the molecule and any complexes it forms with the metal.

This procedure is summarized in Figure 1. The first step is to form the molecule from the elements as an ideal gas at 1 atm, 298 K. The next step is to take the molecule from the vapor state to the ideal liquid state at 1 m concentration, 298 K. The pK values are then used to estimate the free energies of any ionized forms. Note that property estimation at elevated temperatures requires heat capacity data. If such data are available then either of two alternative paths could be followed to correct for temperature.

The first path is to add one more step and take the molecule from 298 K in the aqueous solution to the temperature in the aqueous solution. Various heat capacity information is available for this path.¹⁷ The second method involves taking the molecule in the vapor phase at 298 K to the vapor phase at the desired temperature. The molecule is then moved into the ideal aqueous solution at the desired temperature. This path may be more difficult because of a paucity of data.

An example is presented to demonstrate the estimation procedure using these group contribution techniques. The example shows that EMF-pH diagrams can be generated with organic molecules fairly easily as long as the necessary intermediate properties can be derived. More importantly, the diagram so constructed is consistent with and useful for corrosion prediction.

IRON-IMINODIACETIC ACID SYSTEM

A recent application of EMF-pH diagrams involved the need to identify the cause of excessive corrosion of carbon steel when this alloy was exposed to a waste stream, one major organic component of which is iminodiacetic acid (IDA). Carbon steel corrosion rates of the order of 1 cm/y were measured in this solution in the laboratory. The corrosion rate was an order of magnitude less when this waste was substantially diluted. In the plant environment, addition of this stream to others already being handled successfully by carbon steel was observed to accelerate the corrosion of carbon steel. The question arose as to what component might be causing this increased corrosion. Attention turned to the IDA molecule because it is known to complex with iron.^{18,19} In fact, solid compounds of Fe(II) and IDA have been prepared in the laboratory.²⁰

To accelerate corrosion, IDA must enter into the corrosion mechanism. If a complex between IDA and iron is thermodynamically stable in the environment, then a possible reaction path is present by which such a complex might form. That such a path exists does not necessarily mean that the complex will definitely form. Kinetic information is required to determine if the complex can form and if its creation accelerates corrosion. However, demonstration that such a path exists determines what further experiments are required. Such experiments must demonstrate if IDA can accelerate corrosion and how formation of the complex might be prevented.

The procedure used to interface the EMF-pH diagram with the real world has been discussed previously.^{2,6,13} The diagram is calculated from measured or estimated thermodynamic data and drawn as a function hydrogen ion activity and equilibrium potential. The real world is usually represented by the measured pH and corrosion potential. The interfacing is done by placing the measured pH and steady-state corrosion potential on the diagram. The assumptions are that the measured pH value approximates the calculated hydrogen ion activity, and the measured steady-state corrosion potential is approximately the thermodynamic driving force potential for corrosion product formation. The difference between the actual thermodynamic (pH,potential) coordinate and that derived from this assumption is difficult to estimate. However, the error is minimized by the fact that the axes are actually logarithms (logarithms of hydrogen and electron activities).

Table 1 shows the free energies of formation and standard entropies for the inorganic iron compounds considered.⁹ IDA has been stated to form two dissolved complexes with Fe(II). One complex is uncharged and is of the form Fe(IDA). The other is Fe(IDA)_2^{-2} .²¹ If either of these complexes can be shown to be thermodynamically favored at the pH and corrosion potential in the stream, then a possible path for corrosion involving such species has been shown to exist. Thermodynamic data for these complexes in the standard state of 298 K, aqueous solution, unit activity are nonexistent. Therefore, such data had to be estimated as follows.

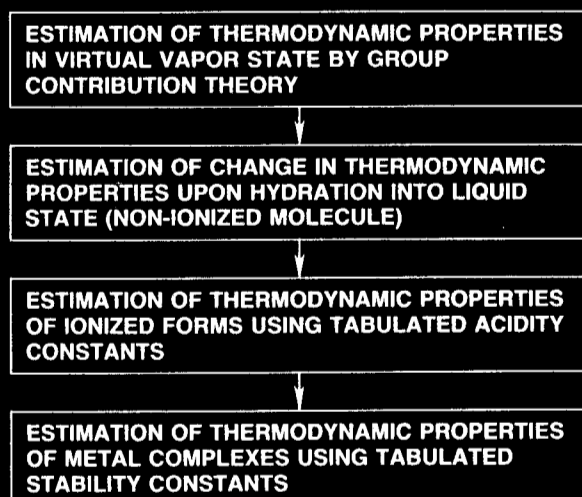


FIGURE 1. Procedure for estimating thermodynamic data for organic complexing agents.

TABLE 1
Thermodynamic Data for Inorganic Iron Compounds⁽¹⁾

Compound	Free Energy of Formation (298 K) (J/mol)	Standard Entropy (298 K) (J/mol-K)
Fe	0.0	2.71 x 10
Fe ₃ O ₄	-1.02 x 10 ⁶	1.46 x 10 ²
Fe ₂ O ₃	-7.42 x 10 ⁵	8.73 x 10
FeOOH	-4.90 x 10 ⁵	6.73 x 10
Fe(OH) ₂ Solid	-4.93 x 10 ⁵	9.24 x 10
Fe(OH) ₃ Solid	-7.14 x 10 ⁵	9.61 x 10
Fe ⁺²	-9.22 x 10 ⁴	-1.07 x 10 ²
FeOH ⁺	-2.74 x 10 ⁵	-2.93 x 10
Fe(OH) ₂ Dissolved	-4.49 x 10 ⁵	3.80 x 10
Fe(OH) ₃	-6.21 x 10 ⁵	4.18 x 10
Fe ⁺³	-1.78 x 10 ⁴	-2.79 x 10 ²
FeOH ⁺²	-2.42 x 10 ⁵	-1.05 x 10 ²
Fe(OH) ₂ ⁻	-4.59 x 10 ⁵	-2.93 x 10
Fe(OH) ₃ Dissolved	-6.61 x 10 ⁵	7.52 x 10
Fe(OH) ₂ ⁻	-8.43 x 10 ⁵	2.51 x 10
Fe ₂ (OH) ₂ ⁺⁴	-4.94 x 10 ⁵	-2.93 x 10 ²
Fe ₂ (OH) ₄ ⁺⁵	-9.69 x 10 ⁵	-4.64 x 10 ²
FeO ₄ ⁻² (?)	-4.67 x 10 ⁵	3.76 x 10

⁽¹⁾Data taken from Reference 8.

TABLE 2
Groups Used to Estimate Thermodynamic Properties of Iminodiacetic Acid (IDA) at 1 atm, 298 K

Group	No. in Molecule	Enthalpy of Formation (J/mol)	Internal Entropy (J/mol-K)
O(CO)(H)	2	-4.86 x 10 ⁵	2.05 x 10 ²
CO(O)(C)	2	-2.94 x 10 ⁵	1.24 x 10 ²
C(H) ₂ (CO)(N)	2 ⁽¹⁾	-5.52 x 10 ⁴	8.20 x 10
N(H)(C) ₂	1	6.44 x 10 ⁴	3.74 x 10

⁽¹⁾C(H)₂(CO)(N) defined to be equivalent to C(H)₂(C)(N). Free energy of formation of IDA = -6.10 x 10⁵ J/mol-K.

In the first step, the IDA molecule was formed in the virtual vapor state of 1 atm, 298 K from its constituent elements using the group contribution theory of Benson.¹⁶ Table 2 shows the groups, the changes in enthalpy upon their formation, and their internal entropy. The change in entropy in forming the IDA molecule was estimated by subtracting the internal entropy of the constituent elements in their standard states from the total internal entropy of the IDA molecule in its virtual state. The free energy of formation of the IDA molecule in the vapor state is obtained simply by

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

(Symbols are defined in the Appendix.)

The next step was to take the IDA molecule from the vapor state into the aqueous solution at 1 m concentration unit activity coefficient. No tabulation of such thermodynamic properties exists for IDA. Therefore, the group contribution method proposed by Cabani, et al¹⁷ was used. As discussed by these authors, these contributions were established by subdividing molecules for which the free energies of hydration are known into groups, each of which is assumed to contribute a constant amount to the thermodynamic property. The groups that form IDA and each of their contributions to the free energy of hydration are shown in Table 3.

Included is the estimated free energy of hydration according to the Cabani, et al rules.¹⁷ This free energy, when added to that for the molecule in its virtual vapor state, yields the free energy of formation of IDA in its un-ionized state at 1 m concentration, 298 K, unit activity coefficient.

This estimated free energy change of hydration does not consider the interaction between the two carboxylic acid groups in the IDA molecule. This interaction could alter the free energy change by about 10⁴ J/mol.¹⁷ However, this error is probably buried within other errors created by the estimation procedure. Neglect of this

TABLE 3
Groups Used to Estimate Free Energy Change of Hydration¹⁷

Group (No.)	Free Energy Change ⁽¹⁾ (J/mol)
COOH (2)	-6.42 x 10 ⁴
CH ₂ (2)	7.4 x 10 ²
NH(C) ₂ (1)	-2.41 x 10 ⁴

⁽¹⁾Free energy change of hydration = -8.68 x 10⁴ J/mol. (Note that a constant value of 1.06 x 10³ J/mol is included.)

interaction should have, at the most, only a small effect on the calculated boundaries for the regions of stability for any IDA complexes.

IDA has three acid-base equilibria. Measured acid-base stability constants are tabulated by Sillen and Martell.²¹ These tabulated stability constants have not been corrected to zero ionic strength. Therefore, they only approximate the equilibrium constants. In the absence of equilibrium constants, these stability constants must be used. The free energy change in forming each ionic species at 298 K was estimated by using each of the three stability constants for IDA in the equation

$$\Delta G = -2.303RT \log_{10}(K) = 2.303RT(\text{pK}) \quad (2)$$

Note that an error of 1 unit in the pK results in an error of ~5000 J/mol or <1% in the free energy. Thus, little error is introduced by substituting stability constants for equilibrium constants. The final free energies of formation of each of the IDA forms and the pH range over which each is the most stable IDA form is shown in Table 4.

TABLE 4
IDA Free Energy Estimates and pH Stability Range at 298 K, 1 atm, Zero Ionic Strength

Species	Free Energy of Formation (J/mol)	pH Stability Range
IDAH ₃ ⁺	-7.07 x 10 ⁵	pH < 1.82
IDAH ₂	-6.97 x 10 ⁵	1.82 < pH < 2.39
IDAH ⁻	-6.83 x 10 ⁵	2.39 < pH < 9.60
IDA ⁻²	-6.29 x 10 ⁵	9.60 < pH

The last step was the estimation of free energies of formation of the dissolved iron-IDA complexes. The procedure is similar to that described above. The measured stability constants for the known complexes are tabulated by Sillen and Martell,²¹ which were again not corrected for ionic strength. These constants tended to be for the formation of the metal-ion complex from the completely ionized form of the organic constituent. Once again, these stability constants were assumed to be equilibrium constants. The free energy change in forming each complex from the metal ions was again estimated by Equation (2). The free energies of formation of the iron-IDA complexes estimated by this procedure are shown in Table 5.

TABLE 5
Free Energy Estimates of Iron-IDA Complexes at 298 K, 1 atm, Zero Ionic Strength

Species	Free Energy of Formation (J/mol)
Fe-(IDA)	-7.53×10^5
Fe-(IDA) ₂ ⁻²	-1.41×10^6

The free energies of formation in Tables 1 through 5 were used to construct the EMF-pH diagram at 323 K. The algorithm for making these calculations has been described previously.¹³ The results at 323 K in the absence and presence of the 0.04 m IDA in the waste solution, as measured by isotachophoresis (pH 6 electrolyte), are shown in Figures 2 and 3. Included are the measured pH and corrosion potential in the waste solution stream containing the IDA. The pH limits of stability for the various IDA species were not corrected for temperature because of a lack of information on the change of each pK with temperature. The correction is probably less than the variation in stability constants with changes in

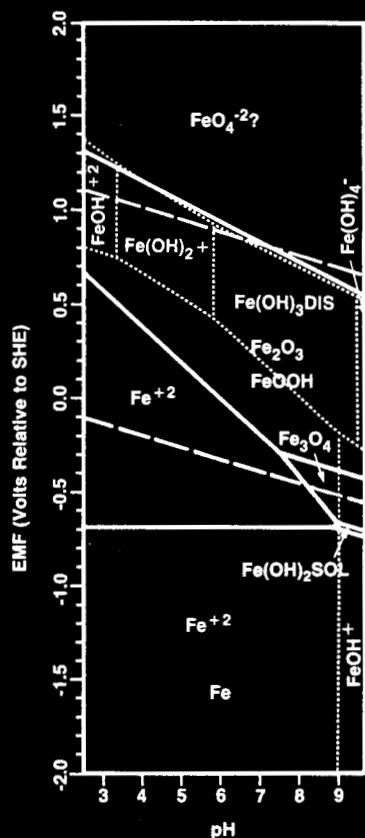


FIGURE 2. EMF-pH diagram for iron at 323 K; dissolved species are at an activity of 10^{-6} .

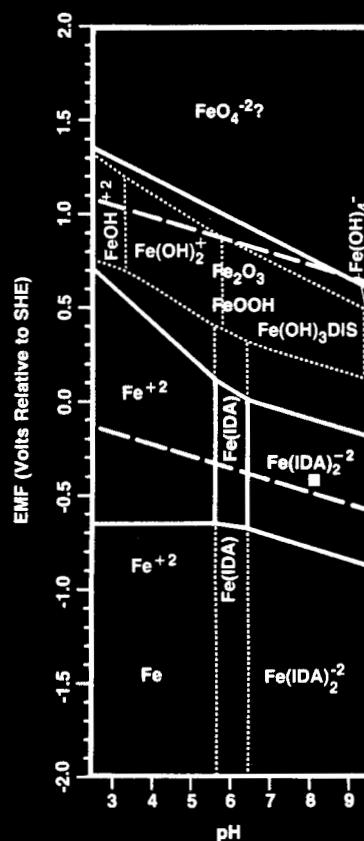


FIGURE 3. EMF-pH diagram for iron with IDA at 323 K; dissolved iron species are at an activity of 10^{-6} . IDA is at an activity of 0.036, and iron-IDA complexes are at an activity of 10^{-5} ; actual solution (■), pH \approx 8, corrosion potential \approx -0.40 V.

supporting electrolyte. The thermodynamic properties of the solid iron species and inorganic iron containing ions were automatically corrected for temperature in the program.¹³ The procedure for iron, iron oxides, and inorganic ions was straightforward, using either measured heat capacities for the solids or the Criss-Cobble Correspondence Principle for the ions²² as modified by Taylor²³ and as described previously.¹³ Such information is lacking for IDA and iron-IDA complexes in solution. Note that neglecting the temperature effect on the properties of IDA and its ions should have a negligible effect on the results because of the expected relative insensitivity of the free energy to temperature over the 25 C range (298 K standard state to 323 K operating temperature).

The results shown in Figures 2 and 3 indicate that an iron-IDA complex is thermodynamically stable at the system conditions. Hence, IDA does provide an additional pathway to a corrosion product. Since the most stable $(\text{FeIDA})_2^{-2}$ or Fe(IDA) product is a dissolved species and not a solid species [e.g., $\text{Fe(OH)}_2\text{SOL}$], the results suggest that this additional reaction pathway could lead to the enhanced corrosion observed. The corrosion potential is near the boundary between the regions of stability of water and hydrogen suggesting that water reduction is the cathodic charge transfer reaction. Obviously, kinetic measurements and solution analyses are required to confirm that IDA does form a complex and does accelerate the corrosion. However, the presence of an iron-IDA complex at the pH and corrosion potential does provide a plausible hypothesis for explaining the high corrosion rates and provides guidance for what further experiments are required.

These results show that having an ability to incorporate organic species that can form complex metal ions on an EMF-pH diagram for that metal greatly increases the versatility of these diagrams as tools for corrosion prediction. The procedure outlined above using group contribution methods provides one reasonable method for such incorporation.

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APPENDIX

List of Symbols

The following is a list of the symbols used throughout this paper:

- ΔG = Change in free energy (J/mol)
 ΔH = Change in enthalpy (J/mol)
 K = Equilibrium constant (dimensionless)
 R = Gas constant (J/mol-K)
 ΔS = Change in entropy (J/mol-K)
 T = Absolute temperature (K)