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Internet: psdomsk@sandia.gov**date:** September 17, 2018**to:** SNL WIPP Records Center
Defense Waste Management Programs**from:** Paul S. Domski*Shelley R. Nelson for 1-9-19***subject:** Memo on the estimation of Pitzer parameters for the $Mg^{2+} / CaEDTA^{2-}$, $Mg^{2+} / MgEDTA^{2-}$, and $Ca^{2+} / EDTA^{4-}$ pairs

This memo documents the estimation of Pitzer parameters for $Mg^{2+} / CaEDTA^{2-}$, $Mg^{2+} / MgEDTA^{2-}$, and $Ca^{2+} / EDTA^{4-}$ pairs. This task builds off the task documented in Domski (2018).

The steps are as follows:

- 1) The QA EQ3/6 database, data0.fmt.R2, aka, DATA0.FM1 is copied to an interim database, DATA0.ED5 in this case, which was updated with the parameters that are being estimated for the task at hand, and any supporting parameters.
- 2) The Python script specific to the problem, and which calls the parameter optimization script "EQ3CodeModule.py" (Kirchner, 2012), is executed and the specified parameters are estimated.
- 3) The output of the Python script, a text file named "results.txt", which consists of the parameter estimates and the calculated residual, is evaluated in Excel to determine the parameter(s) which corresponds to the smallest value of the residual.
- 4) The fitted parameters are documented in a memo to records.

Fitting and Auxiliary Parameters

Three parameters were estimated for this task, $\beta^{(1)}$ for the $Mg^{2+} / CaEDTA^{2-}$, $Mg^{2+} / MgEDTA^{2-}$ pairs, and $\beta^{(0)}$ for $Ca^{2+} / EDTA^{4-}$ pair. The parameters were estimated by use of the inverse method(s) implemented in the Python script "EQ3CodeModule.py" (Kirchner, 2012).

A clean copy of the QA approved database *Data0.FM1* was copied to interim database *Data0.ED5* and the following parameter data blocks for the fitting parameters and supporting parameters were added, or edited as noted. The parameter datablocks that existed in *Data0.FM1* and that were edited for this task were edited because more up to date references for these parameters had become available.

The data blocks are as follows:

Updated Aqueous species – All species below were updated

```

+-----+
CaEDTA--                               CaClOH12O8N2--
charge = -2.0
****
5 element(s):
10.0000 C                               1.0000 Ca                               12.0000 H

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```

      2.0000 N          8.0000 O
****
      3 species in aqueous dissociation reaction:
      -1.0000 CaEDTA--          1.0000 Ca++
      1.0000 EDTA----
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
      No_Data -12.69000 No_Data No_Data
      No_Data No_Data No_Data No_Data
*Source: Hummel(2005)
+-----+
H4EDTA(aq)          H4C10H12O8N2(aq)
      charge = 0.0
****
      4 element(s):
      10.0000 C          16.0000 H          2.0000 N
      8.0000 O
****
      3 species in aqueous dissociation reaction:
      -1.0000 H4EDTA(aq)          4.0000 H+
      1.0000 EDTA----
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
      No_Data -23.4200 No_Data No_Data
      No_Data No_Data No_Data No_Data
* Source: Hummel et al. (2005)
+-----+
H3EDTA-          H3C10H12O8N2-
      charge = -1.0
****
      4 element(s):
      10.0000 C          15.0000 H          2.0000 N
      8.0000 O
****
      3 species in aqueous dissociation reaction:
      -1.0000 H3EDTA-          3.0000 H+
      1.0000 EDTA----
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
      No_Data -21.19 No_Data No_Data
      No_Data No_Data No_Data No_Data
* Source:Hummel et al. (2005)
+-----+
H2EDTA--          H2C10H12O8N2--
      charge = -2.0
****
      4 element(s):
      10.0000 C          14.0000 H          2.0000 N
      8.0000 O
****
      3 species in aqueous dissociation reaction:
      -1.0000 H2EDTA--          2.0000 H+
      1.0000 EDTA----
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
      No_Data -18.0400 No_Data No_Data
      No_Data No_Data No_Data No_Data
* Source:Hummel et al. (2005)
+-----+
HEDTA---          HC10H12O8N2---
      charge = -3.0
****
      4 element(s):
      10.0000 C          13.0000 H          2.0000 N
      8.0000 O
****

```

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3 species in aqueous dissociation reaction:
-1.0000 HEDTA--- 1.0000 H+
1.0000 EDTA----

*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
No_Data -11.2400 No_Data No_Data
No_Data No_Data No_Data No_Data
* Source:Hummel et al. (2005)

Solid phase Ca₂EDTA.7H₂O(s) – Supporting parameter

Ca2EDTA.7H2O(s) Ca2C10H12O8N2.7H2O
sp.type = solid
* EQ3/6 = xxx
revised = 26-Sept-2012
* mol.wt. = 570.5008 g/mol
V0PrTr = 0.000 cm**3/mol [source:]

5 element(s):
10.0000 C 26.0000 H 15.0000 O
2.0000 Ca 2.0000 N

4 species in aqueous dissociation reaction:
-1.0000 Ca2EDTA.7H2O(s) 2.0000 Ca++
1.0000 EDTA---- 7.0000 H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
500.0000 -16.8100 500.0000 500.0000
500.0000 500.0000 500.0000 500.0000
*Source: As documented in Domski (2018)

Ca²⁺ - EDTA⁴⁻ - fitting parameter

Ca++ EDTA----
alpha(1) = 1.4
alpha(2) = 12.0
beta(0)
a1 = 0.0
a2 = 0.
a3 = 0.
a4 = 0.
beta(1)
a1 = 0.
a2 = 0.
a3 = 0.
a4 = 0.
beta(2)
a1 = 0.
a2 = 0.
a3 = 0.
a4 = 0.
Cphi:
a1 = 0.0
a2 = 0.
a3 = 0.
a4 = 0.
* Source: beta(0) fitting parameter as directed by Charles Oakes

Mg²⁺ - CaEDTA²⁻ - fitting parameter

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```

Mg++                                CaEDTA--
alpha(1) = 1.4
alpha(2) = 12.0
beta(0)
  a1 = 0.0
  a2 = 0.
  a3 = 0.
  a4 = 0.
beta(1)
  a1 = 0.0
  a2 = 0.
  a3 = 0.
  a4 = 0.
beta(2)
  a1 = 0.
  a2 = 0.
  a3 = 0.
  a4 = 0.
Cphi:
  a1 = 0.0
  a2 = 0.
  a3 = 0.
  a4 = 0.
* Source: beta(1) fitting parameter as directed by Charles Oakes
+-----+

```

Mg²⁺ - MgEDTA²⁻ - fitting parameter

```

+-----+
Mg++                                MgEDTA--
alpha(1) = 1.4
alpha(2) = 12.0
beta(0)
  a1 = 0.0
  a2 = 0.
  a3 = 0.
  a4 = 0.
beta(1)
  a1 = 0.0
  a2 = 0.
  a3 = 0.
  a4 = 0.
beta(2)
  a1 = 0.
  a2 = 0.
  a3 = 0.
  a4 = 0.
Cphi:
  a1 = 0.0
  a2 = 0.
  a3 = 0.
  a4 = 0.
* Source: beta(1) fitting parameter as directed by Charles Oakes
+-----+

```

The data used for fitting was taken from Table 3 of Xiong (2018), where the average of the data measured was used to create EQ3NR input files. A python script was created (*Mg_EDTA.py*) which directed the fitting parameters, EQ3NR input files, and interim database to be in fitting the parameters.

There were issues fitting the data, the EQ3NR input file for the 2.5 molal MgCl₂ would not converge regardless of which database was used. Every effort was made to work with this data and include it in the fitting process, but no solution was found. As a result this data was excluded and only the data up to 2.0 molal MgCl₂ was included in the fitting exercise.

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The fitting results are listed in Table 1. EQ6 simulations using the fitted parameters are shown in Figures 1 and 2, for the MgCl_2 matrix solution. Figure 1 shows the fit of the simulated total calcium versus MgCl_2 and the fit is quite good. However, Figure 2 shows the fit of the simulated pmH to the measured versus MgCl_2 concentration, and the fit is not ideal. The reason for the disparity is not known, but could be due to a combination of effects, among which may include measurement error, thermodynamic uncertainty, and the EQ6 conceptual model representing an idealized system. While the fit appears to be not ideal the maximum difference between the measured pmH and the simulated is approximately 0.4 pH units which is not really that great. Therefore, based on the analysis the fitted parameters are considered to adequately represent the chemical system.

Results

Table 1. Results of fitting.

Ion Pair	$\beta^{(0)1}$	$\beta^{(1)1}$	$C^{\phi 1}$	Log K	Residual	Python Script	Results file ²
$\text{Mg}^{2+}/\text{CaEDTA}^{2-}$	0.0	7.2111	0.0	-	0.0109	Mg_EDTA.py	Mg-EDTA_Results.xlsx
$\text{Mg}^{2+} / \text{MgEDTA}^{2-}$	0.0	7.2760	0.0	-			
$\text{Ca}^{2+} / \text{EDTA}^{4-}$	2.4776	0.0	0.0	-			

1- parameter values of 0.0 were not fit

2 – files may be found at: [/nfs/data/CVSLIB/WIPP_EXTERNAL/APPENDIXGEOCHEM/Files](#)

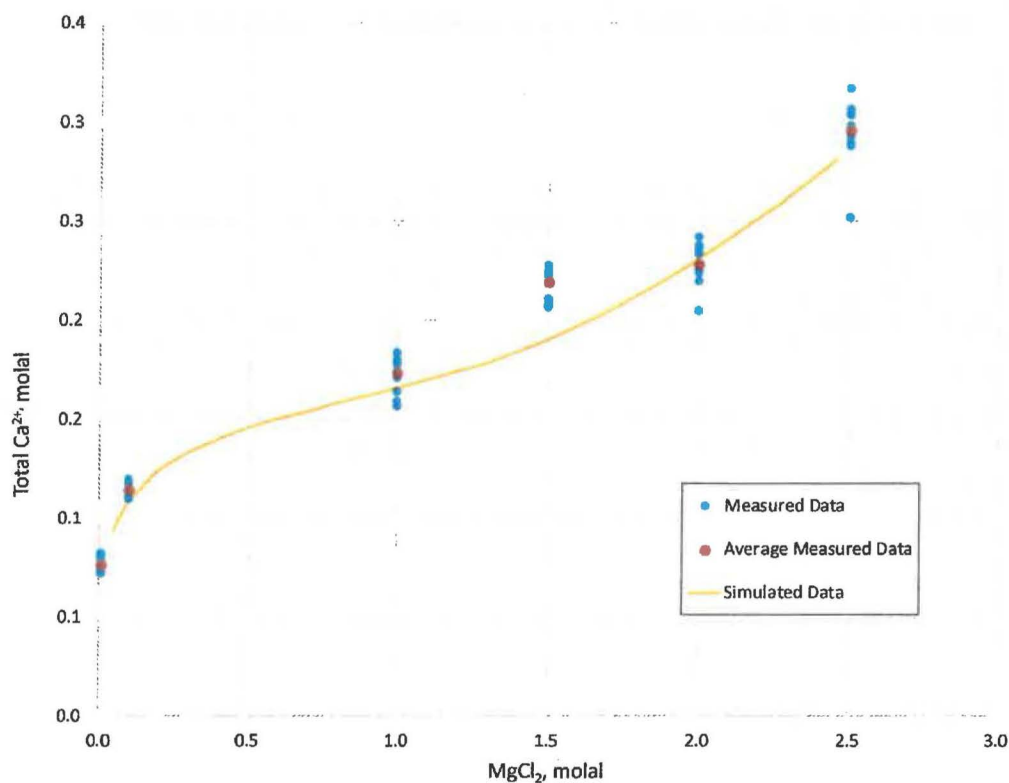


Figure 1. EQ6 simulation comparing the measured total Ca concentration to the simulated Ca concentration as a function of MgCl_2 concentration.

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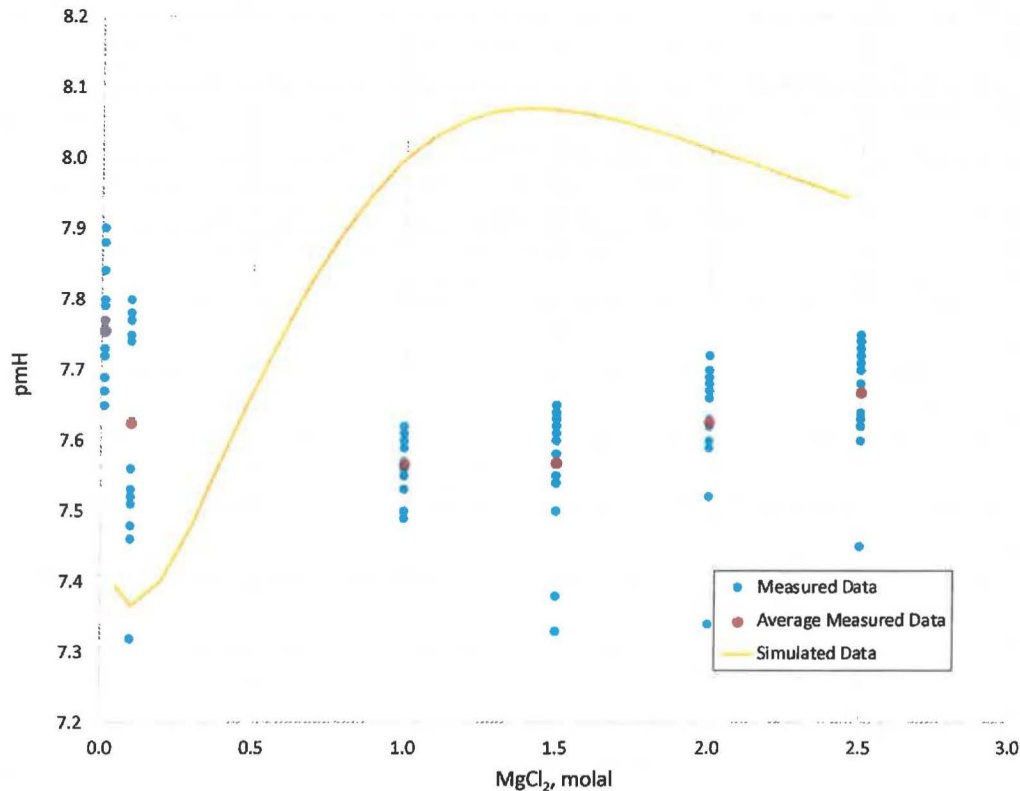


Figure 2. EQ6 simulation comparing the measured pmH to the simulated pmH as a function of MgCl₂ concentration.

References

- Domski, P.S. 2018. Memo on the estimation of Pitzer parameters for the Mg²⁺ / CaEDTA²⁻, Mg²⁺ / MgEDTA²⁻, and Ca²⁺ / EDTA⁴⁻. ERMS# Carlsbad, NM: Sandia National Laboratories.
- Kirchner, T.B., 2012. User's Manual for The EQ3CodeModule Version 1.00. Carlsbad, NM: Sandia National Laboratories. ERMS 557360.
- Xiong, Y.-L. 2018. "Experimental determination of solubilities of lead oxalate (PbC₂O₄), di-calcium ethylenediaminetetraacetic acid hydrate (Ca₂EDTA•7H₂O(s)) in MgCl₂-H₂O system, and earlandite (Ca₃[C₃H₅O(COO)₃]₂•4H₂O) in NaCl-H₂O and MgCl₂-H₂O systems, and their respective Pitzer interaction parameters, Revision 3, Supersedes ERMS 567810. Carlsbad, NM: Sandia National Laboratories. ERMS: 570088.

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