570202

Sandia National Laboratories

Operated for the U.S. Department of Energy by
Sandia Corporation

4100 National Parks Highway
Carlsbad, NM 88220

Phone: (575) 234-0056
Fax: (575) 234-0061
Internet: psdomsk@sandia.gov

date: July 18, 2018

to: SNL WIPP Records Center
Defense Waste Management Programs

from: Paul S. Domski Shelly R. Nielsen for

subject: Memo on the estimation of the solubility product (Log K_{sp}) for $Ca_2EDTA.7H_2O$, and Pitzer parameters for the Na+ / $CaEDTA^{2-}$ pair

This memo documents the estimation of the solubility product (Log Ksp) for $Ca_2EDTA.7H_2O$, and Pitzer parameters for the Na^+ / $CaEDTA^{2-}$ pair. The steps are as follows:

1) The QA EQ3/6 database, data0.fmt.R2, aka, DATA0.FM1 is copied to an interim database, DATA0.ED4 in this case, which is 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, $LogK_{sp}$ for $Ca_2EDTA.7H_2O$, and $\beta^{(0)}$ and $\beta^{(1)}$ for the Na^+ / $CaEDTA^{2-}$ 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.ED4* 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 Aqeous species – All species below were updated

```
+----------------------------------------------------------------
CaEDTA--                  CaC10H12O8N2--
     charge   =   -2.0
****
     5 element(s):
     10.0000 C              1.0000 Ca           12.0000 H
      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
****
     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)
+---------------------------------------------------------------
```

Aqeous species - This datablock was added

```
+---------------------------------------------------------------
NaEDTA---                  NaC10H12O8N2---
     charge  =  -3.0
****
     5 element(s):
     10.0000 C             12.0000 H             2.0000 N
      8.0000 O              1.0000 Na
****
     3 species in aqueous dissociation reaction:
    -1.0000  NaEDTA---                  1.0000 Na+
     1.0000  EDTA----
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
        No_Data  -2.80000   No_Data   No_Data

        No_Data   No_Data   No_Data   No_Data
* Source:Hummel et al. (2005)

+---------------------------------------------------------------
```

Solid phase $Ca_2EDTA.7H_2O(s)$ – Fitting 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: This document
+---------------------------------------------------------------
```

Pitzer parameters for Na^+ - $CaEDTA^{2-}$ - fitting parameter

```
+---------------------------------------------------------------
Na+                        CaEDTA--
  alpha(1) = 2.0
  alpha(2) = 12.0
  beta(0)
    a1 = 0.185
    a2 = 0.
    a3 = 0.
```

```
    a4 = 0.
  beta(1)
    a1 = 2.405
    a2 = 0.
    a3 = 0.
    a4 = 0.
  beta(2)
    a1 = 0.
    a2 = 0.
    a3 = 0.
    a4 = 0.
  Cphi:
    a1 = 0.
    a2 = 0.
    a3 = 0.
    a4 = 0.
* source:    This document, fit beta(0) and beta(1)
+------------------------------------------------------------------
```

Updated Pitzer parameters

```
+------------------------------------------------------------------
Na+                          HEDTA---
  alpha(1) = 2.0
  alpha(2) = 12.0
  beta(0)
    a1 = 0.590
    a2 = 0.
    a3 = 0.
    a4 = 0.
  beta(1)
    a1 = 5.31
    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: Felmy (2003)
+------------------------------------------------------------------
Na+                          EDTA----
  alpha(1) = 2.0
  alpha(2) = 12.0
  beta(0)
    a1 = 1.10
    a2 = 0.
    a3 = 0.
    a4 = 0.
  beta(1)
    a1 = 15.6
    a2 = 0.
    a3 = 0.
    a4 = 0.
  beta(2)
    a1 = 0.
    a2 = 0.
    a3 = 0.
    a4 = 0.
  Cphi:
```

```
    a1 = 0.001
    a2 = 0.
    a3 = 0.
    a4 = 0.
* Source: Felmy (2003)
+--------------------------------------------------------------------
```

The data used for fitting was taken from Table 4 of Xiong (2018), where the average of the most aged data, the data measured at day 1431, was used to create EQ3NR input files. A python script was created (*Na_EDTA_2.py*) which directed the fitting parameters, EQ3NR input files, and interim database.

The results are listed in Table 1. EQ6 simulations using the fitted parameters are shown in Figures 1 and 2, for the NaCl matrix solution. Figure 1 shows the fit of the simulated total calcium versus NaCl and the fit is quite good. However, Figure 2 shows the fit of the simulated pmH versus NaCl concentration, and the fit is relatively good. The EQ6 simulation at low NaCl concentrations is off by approximately 0.2 pH units compared to the measured pmH values. The reason for this disparity is likely due to a combination of effects, among which may include measurement error, thermodynamic uncertainty, and the EQ6 conceptual model. However, based on the analysis the fitted parameters are considered to adequately represent the chemical system.

Results

Table 1. Results of fitting.

Ion Pair	$\beta^{(0)}$	$\beta^{(1)}$	$C^{\phi 1}$	Log K	Residual	Python Script	Results file[2]
$Ca_2EDTA.7H_2O(s)$	-	-	-	-16.81	0.0004	Na_EDTA_2.py	*Ave_1431_Results.xlsx*
Na^+ / $CaEDTA^{2-}$	0.185	2.405	0.0	-			

1- C^{ϕ} was not a fitting parameter

2 – files may found at: /nfs/data/CVSLIB/WIPP_EXTERNAL/APPENDIXGEOCHEM/Files

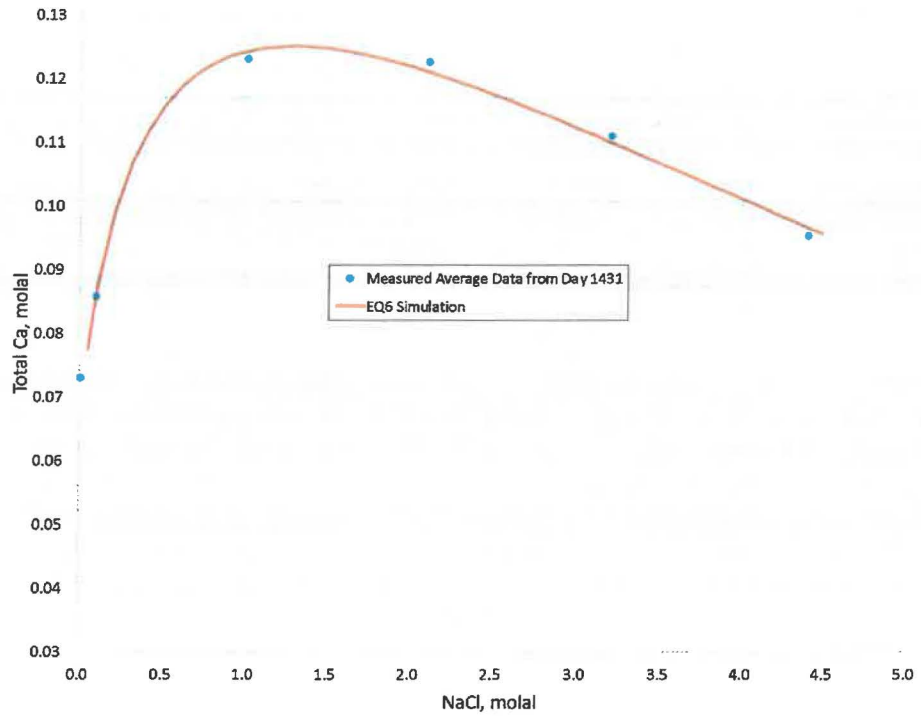

Figure 1. EQ6 simulation comparing the measured total Ca concentration to the simulated Ca concentration as a function of NaCl concentration.

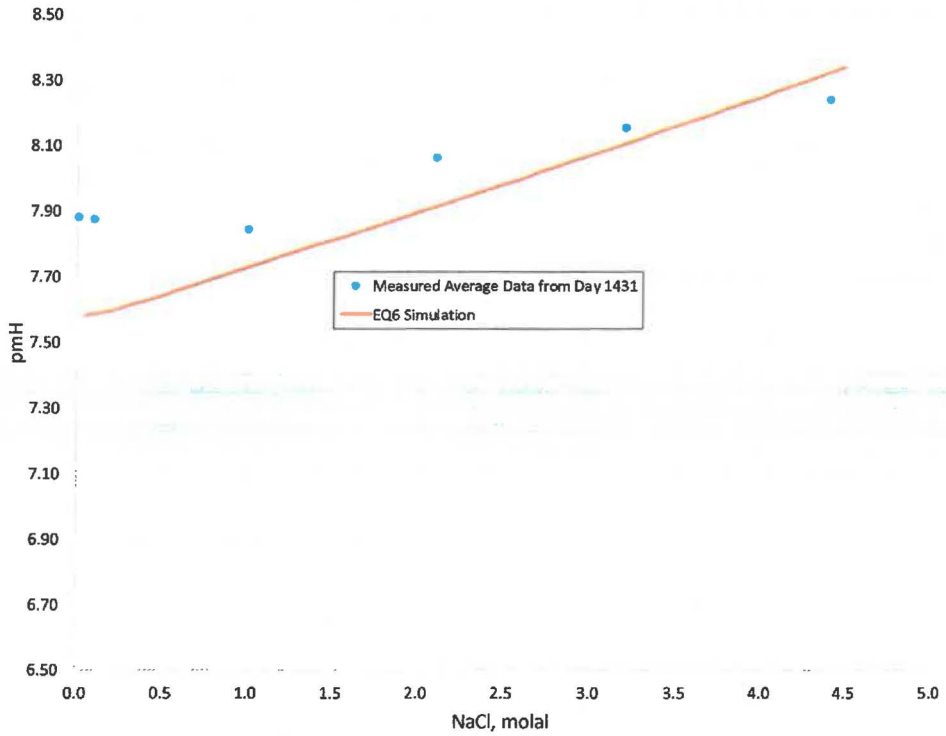

Figure 2. EQ6 simulation comparing the measured pmH to the simulated pmH as a function of NaCl concentration.

References

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.