OLI Adsorption Manual

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Table of Contents

Chapter 1 Introduction

This manual explains OLI's treatment of ion exchange, surface complexation, and molecular adsorption. The purpose is to describe OLI's adsorption models, describe database entries needed for adsorption and how to use non-linear regression to find them, and to provide some detailed examples of adsorption simulations.

This manual is a stand-alone addition to OLI's OLI Engine and OLI ESP User's Manual and does not cover all the details of other OLI software, so some previous familiarity with OLI's ESP process and OLI engine is required for greater understanding of this manual.

Type of adsorption

There are currently three types of adsorption[1] handled by OLI's software:

Ion exchange

- Charged surface – all negative (cation exchange) or all positive (anion exchange)
- All sites occupied resulting in effectively neutral surface combination

Surface complexation

- Charged surface – all negative (HFO-)
- Some sites occupied, some not occupied
- Sites occupied with cations, anions or complexes resulting in positive, negative or neutral sites

Molecular adsorption

- Neutral surface
- Some sites occupied, some not occupied
- Sites occupied with neutral molecules

[1] The word *Adsorption* as used in this document collectively covers all three types of adsorption phenomena. Specific types of adsorption (ion exchange, surface complexation, or molecular adsorption) will be used when referring to specific adsorption types.

Chapter 2 Adsorption Models

Ion Exchange

- Charged Surface - all negative (cation exchange) or all positive (anion exchange)
- All sites occupied resulting in effectively neutral surface combination

Equilibrium

Ions: A^{Z_A}, B^{Z_B}

Medium: X^{Z_X}

$$\frac{1}{Z_B}\left[B^{Z_B}X_{Z_B}^{Z_X}\right]+\frac{1}{Z_A}\left[A^{Z_A}\right]=\frac{1}{Z_B}\left[A^{Z_A}X_{Z_A}^{Z_X}\right]+\frac{1}{Z_A}\left[B^{Z_B}\right]$$

$$K_{AB}=\frac{\left(f_{A-X}M_{A-X}\right)^{1/Z_A}\left(\gamma_B m_B\right)^{1/Z_B}}{\left(f_{B-X}M_{B-X}\right)^{1/Z_B}\left(\gamma_A m_A\right)^{1/Z_A}}$$

Where

Z_A, Z_B = charges of species A and B, respectively.
>0 = cation exchange, <0 = anion exchange

f_{i-x} = activity coefficient of ionic species i in "solid" phase

γ_i = activity coefficient of ionic species i in aqueous phase

M_{i-x} = molar concentration of ionic species i in "solid" phase

m_i = molar concentration of ionic species i in aqueous phase

K_{ij} = thermodynamic equilibrium constant between ions i and j

Example

$$NaClay + {}^1/_2\,Ni^{+2} \rightleftharpoons {}^1/_2\,NiClay_2 + Na^{+1}$$

Where

$A = Ni \qquad Z_A = +2$

$B = Na \qquad Z_B = +1$

$X = Clay$

$$K_{\frac{Ni}{Na}}=\frac{\left(f_{NiClay_2}M_{NiCLAY2}\right)^{1/2}\left(\gamma_{Na}m_{Na}\right)}{\left(f_{NaClay}M_{NaClay}\right)\left(\gamma_{Ni}m_{Ni}\right)^{1/2}}$$

The equilibrium constant:

$$\log(K)=C_1+\frac{C_2}{T}+C_3T+C_4T^2$$

Parameters C_1, C_2, C_3, C_4

Activity coefficient of the “solid” phase:
OLI has two activity coefficient models of the “solid” phase. One is the Margules model, the other is Wilson’s model.

The Margules model (three parameters Λ_{ij}, Λ_{ji}, D)

$$Ln(\gamma_i) = \left[\Lambda_{ij} + 2x_i\left(\Lambda_{ji} - \Lambda_{ij} - D\right) + 3x_i^2 D\right]x_j^2$$
$$Ln(\gamma_j) = \left[\Lambda_{ji} + 2x_j\left(\Lambda_{ij} - \Lambda_{ji} - D\right) + 3x_j^2 D\right]x_i^2$$

The Wilson’s model (two parameters Λ_{ij}, Λ_{ji})

$$\ln f_k = -\ln\left(\sum_j x_{j-s}\Lambda_{kj}\right) + z_k \sum_i \frac{x_{i-s}}{z_i}\left(1 - \frac{\Lambda_{ik}}{\sum_j x_{j-s}\Lambda_{ij}}\right)$$

Surface complexation

- Charged surface – all negative (HFO-)
- Some sites occupied, some not occupied
- Sites occupied with cations, anions or complexes resulting in positive, negative or neutral sites

OLI has four surface complexation models: Nonelectrostatic model, constant capacitance model, the double layer model, and triple layer model. Their corresponding databanks are SCNEM, SCCCM, SCDLM, and SCTLM respectively. The basis of the OLI surface complexation model is the diffuse double layer model and the database SCDLM database contains entries for complexation on hydrous ferrous oxide.

If the complexation reaction of interest is not included in the databank, it must be entered by means of a private databank. The following steps are recommended

1. Write the complexation reaction stoichiometry
   OLI notation: -CPM is a neutral complexed form
   -CPI is a charged (positive or negative) complexed form
   For example,
   Reaction: H2OHFO1CPI = HION + HOHFO1CPM
   H2OHFO1CPM is neutral
   HOHFO1CPI is charged +1
2. Determine the surface properties (e.g. surface site density, surface site area,…)
3. Determine the equilibrium constant for the complexation reaction
4. Create a private databank including any new species which are in the reaction.

Hydrous Ferric Oxide

- Structure - crystalline iron oxide (goethite: I-FeOOH) (Dzombak & Morel, section 5.1, pages 89-90)
  'HFOn' species: $Fe\text{-}O^{+}$ - MW = 71.8464 (Fe: 55.847; O: 15.9994)
  n = 1 for Type 1, high affinity cation binding sites
  n = 2 for Type 2, total reactive sites

- Surface Area - estimated specific surface area = 600 m^2/g
  (Recommended by Davis et al.; Dzombak & Morel, section 5.2, pages 90-91)

- Site Densities (Dzombak & Morel, section 5.3, pages 92-95)
  Type 1 (high affinity cation binding sites) = 0.005 mole/mole solid
  Type 2 (total reactive sites) = 0.2 mole/mole solid
  For -HFO1IN moles inlet (the amount of actual reactive surface), the total solid present is -HFO1IN/0.005.
  Since the solid contains both sites, the total solid is also -HFO2IN/0.2.
  Thus, -HFO1IN/.005 = -HFO2IN/.2

and once one is determined, the other must be determined on this basis.

Surface Charge Density

$$\sigma = \frac{F}{A * S} * \sum z_i * C_i$$ (Dzombak & Morel, Figure 2.1, p 11)

where σ = surface charge density, coul/m^2
F = Faraday's Constant, 96485 coul/mole
A = specific surface area, m^2/g
S = solid concentration, gm solid/kg H2O
z_i = charge of Complex Species i
C_i = concentration of complex species i, mole/kg H2O

Thus,

S = -IN flow (gmole sites) * MW (gm solid/gmole solid) = gm solid/kg H2O
Surf Site Dens (gmole sites/gmole solid) * H2O (kg H2O)

Potential at Surface

$$\sigma = \left(8 * R * TK * \varepsilon * \varepsilon_o * I * 10^3\right)^{1/2} * \sinh\left(\frac{Z * \Psi * F}{2 * R * TK}\right)$$ (Dzombak & Morel, Eqn 2.2, p 12)

where σ = surface charge density, coul/m^2
R = gas constant, 8.314 J/mole-K = 8.314 coul-V/mole-K
TK= temperature, K
M = dielectric constant of water at TK
M_o= permittivity of free space, 8.854E-12
I = ionic strength, mol/m^3
Z = valence, unitless
Ψ = potential at surface, V
F = Faraday's Constants, 96485 coul/mole

$\left(\frac{Z * \Psi * F}{2 * R * TK}\right)$ = unitless

$\left(8 * R * TK * e * e_o * I * 10^3\right)$ = (coul/m^2)^2

Since $\sinh^{-1}(x) = \log_e\left[x + \left(x^2 + 1\right)^{1/2}\right]$

$$\frac{Z * \Psi * F}{2 * R * TK} = \log_e\left[\frac{\sigma}{\left(8000 * R * TK * \varepsilon * \varepsilon_o * I\right)^{1/2}} + \left\{\frac{\sigma^2}{8000 * R * TK * \varepsilon * \varepsilon_o * I} + 1\right\}^{1/2}\right]$$

$$\Psi = \frac{TK}{Z * 5802.6} \log_e \left[\frac{\sigma}{7.674 * 10^{-4} * (\varepsilon * TK * I)^{1/2}} + \left\{ \frac{\sigma^2}{5.889 * 10^{-7*} * \varepsilon * TK * I} + 1 \right\}^{1/2} \right]$$

and

$$K^{int} = K^{app} * \exp\left[\frac{\Delta Z * F * \Psi}{R * TK} \right]$$

where K^{int} = intrinsic equilibrium constant
K^{app} = apparent equilibrium constant
$-Z$ = valence change in surface complexation reaction

Dielectric Constant of Water

The dielectric constant of liquid water (ε) is computed along the saturation line from the Uematsu-Franck equation (J. Phys. Chem. Ref. Data., 1980, 9, 1291). The dielectric constant is a function of temperature and density.

Molecular adsorption

- Neutral surface
- Some sites occupied, some not occupied
- Sites occupied with neutral molecules

Molecular adsorption is modeled in the same manner as ion exchanges, except that the medium is not charged, it is neutral.

Molecular adsorption equilibrium:

$$A + X \leftrightarrow AX$$

Where

A is solute (-AQ species)
X is adsorbent (such as activated carbon)
AX is adsorbed combination

Molecular adsorption equilibrium constant:

$$K_{ADS} = \frac{f_{AX} M_{AX}}{\gamma_A m_A f_X M_X}$$

Where

$m_{A,}$ aqueous concentration, solute, gmole/L
M_X, solid solution concentration, adsorbent, gmole/kg solid
M_{AX}, solid solution concentration, adsorbed combination, gmole/kg solid
γ_A , aqueous activity coefficient
f_X, f_{MX}, solid solution activity coefficient

Chapter 3 Database entries

Adsorption species lists

The “Quick List” facility can be used to display or save to a file of the current adsorption species that are currently in the OLI database. A full description of this facility appears in the Databank Chapter of the OLI Users Manual.

Method: initially, the database be searched (e.g., PUBLIC, GECOCHEM, ets.) must be specified followed by the relevant chapter on the succeeding screen. The action Key is then used and the Reports facility chosen. (Note: when using the Experimental or Literature Databook chapters the required section must be specified prior to using the Action Key).

From the report type list displayed the “Quick Lists” option is specified. An index of data items available for reporting from the particular working chapter is then shown. The user can select the specific information to be reported using the Arrows and <Space Bar> keys. (Note: a maximum of 10 items to be reported from a chapter can be selected).

On completing the report item definition and pressing the Enter Key, the user then specifies for which species the report will be made. The species to be reported can then be specified, normally using a wildcard entry. Optionally, the user can use the Action Key and choose the Search facility, to change the way the species in the report are located (e.g. “By Species Name” instead of “By Formula”).

The procedure for producing a species specific data report is summarized in the schematic diagram, Report Options.

Output Choices: reports are sent to the screen by default. Alternately, a report can be sent to a disk file or to the printer by using the Action Key and choosing the Output facility.

Report Options: the “Quick Lists” options automatically assign headings to a report, determines whether the report will be presented in Row (>80 characters) or (<80 characters) format, and uses the internal order of the data to determine the data order in a report. The options facility, when implemented, will allow the user to override the Quick List defaults.

Type	Search for
Ion Exchange	*SOL
Molecular Adsorption	*SOL
Surface Complexation	*CPI and *CPM

Ion Exchange

Database surface species entries

Ion exchange database entries are located in the Sorption chapter by chemical species interaction pair names. There are four types of databases entries:

1. molecular weight of HION+Medium
2. equilibrium constant
3. three-constant Margules interaction parameters or two-constant Wilson's interaction parameters. Note: Either Margules model or Wilson's model parameters are provided for one interaction.
4. equilibrium equation

Ion exchange data example:

```
**BASE LEVEL  0
NAME KCLINOPTSOL      NACLINOPTSOL
**INTE LEVEL  1
MOLW 490.2
K   1.471        0.0         0.0         0.0
WILS 1.323       2.226
EQUA NACLINOPTSOL+KION=KCLINOPTSOL+NAION
```

In this example,
Medium: CLINOPTSOL
Chemical species interaction pair names: NACLINOPTSOL and KCLINOPTSOL
Molecular weight of HION + Medium: 490.2
Equilibrium constant: 1.471
Wilson's model parameters: 1.323 and 2.226
Equilibrium equation:

$$NaCLINOPTSOL + K^+ = KCLINOPTSOL + Na^+$$

Surface complexation

Database surface species entries

Surface complexation parameters are located in the species chapter-solid phase section of the OLI database.

Species surface complexation lines:
SUR1 - surface site density, mole of site/mole solid
SUR2 - surface site density factor
=1.0 for site to be used I computation of solid concentration
=0.0 for site NOT to be used in computation of solid concentration
SUR3 - specific surface site area. M2/gm
SUR4 - solid molecular weight, gm/mole
SUR5 - surface material balance group
SUR6 - charge of the species

Total solid surface area =
Sum {mole site i * MW i * site i density factor * spec surface area i / site density i}

Material Balance Groups

	Matl Code	Name	Charge	MW
Type 1 site:	812	HFO1(-1)	-1	71.8464
Type 2 site:	813	HFO2(-1)	-1	71.8464

'HFO1(-1)' = '≡Fe^{s}'
'HFO2(-1)' = '≡Fe^{w}'

Database entry example:

Take H2OHFO1CPI and H2OHFO2CPI species in the SCDLM databank as an example.

The species H2OHFO1CPI and H2OHFO2CPI are the same species except different surface site density, respectively.

The molecular weights are a sum of the surface MW (HFO, 71.8464), 2 hydrogen atoms (1.008 each) and 1 oxygen atom (15.9994). the material code (MATC and STOI) reflect the same.

The KFIT line represents the $\log_{10}(K^{int})$.

```
**BASE LEVEL  0
NAME H2OHFO2CPI
**GENE LEVEL  1
MOLW 89.861801
```

MATC 813 21 1
STOI 1 1 2
**SOLI LEVEL 1
GREF -4.888200E+05
HREF -5.595700E+05
SREF 60.3801
VREF 2.082000E-05
CPRE 74.999901
EQUA H2OHFO2CPI=HION+HOHFO2CPM
KFIT -7.29
SUR1 0.2
SUR2 1
SUR3 600
SUR4 88.853798
SUR5 813
SUR6 1

**BASE LEVEL 0
NAME H2OHFO1CPI
**GENE LEVEL 1
MOLW 89.861801
MATC 812 21 1
STOI 1 1 2
**SOLI LEVEL 1
GREF -4.888200E+05
HREF -5.595700E+05
SREF 60.3801
VREF 2.082000E-05
CPRE 74.999901
EQUA H2OHFO1CPI=HION+HOHFO1CPM
KFIT -7.29
SUR1 5.000000E-03
SUR2 1
SUR3 600
SUR4 88.853798
SUR5 812
SUR6 1

Equilibria

Surface acidity equilibrium – equation a1 (Dzombak & Morel, Table 2.1 p17)

$$\left(\equiv Fe-O-H_2^+\right) \leftrightarrow H^+ + \left(\equiv Fe-O-H^0\right) \qquad -Z = -1$$

Equilibrium Relationship:

$$\left(\equiv Fe-O-H_2{}^+\right) = \left(H^+\right) * \left(\equiv Fe-O-H^o\right) * \exp\left(\frac{\Delta Z * F * \Psi}{R * T}\right) * \frac{1.0}{K_{a1}{}^{\text{int}}}$$

Since $-Z = -1$,

$$\frac{K_{a1}^{\text{int}}}{\exp\left(\frac{-F*\Psi}{R*T}\right)} = \frac{\left(H^+\right)\left(\equiv Fe-O-H^o\right)}{\left(\equiv Fe-O-H_2{}^+\right)}$$

$$K_{a1}{}^{app} = \frac{K_{a1}^{\text{int}}}{\exp\left(\frac{-F*\Psi}{R*T}\right)} = \frac{\left(H^+\right)\left(\equiv Fe-O-H^o\right)}{\left(\equiv Fe-O-H_2{}^+\right)}$$

(Best Estimate $\log_{10}\left(K_{a1}{}^{\text{int}}\right) = -7.29$

Molecular adsorption

Database surface species entries

Molecular adsorption database entries are located in the Sorption chapter by chemical species interaction pair names. There are four types of database entries:

1. molecular weight of HION + Medium
2. Equilibrium constant
3. Three-constant Margules interaction parameters or two-constant Wilson's interaction parameters. Note: Either Margules model or Wilson's model parameters are provided for one interaction.
4. Equilibrium equation.

Database entry example:

Here is an example of database entries of molecular adsorption interaction: Carbon adsorption of Chlorodibromomethane

```
**BASE LEVEL  0
NAME BR2CLMECARBSOL    CARBSOL
**INTE LEVEL  1
MOLW 4376
K    -5.55641       0.0          0.0          0.0
MARG -1.44203       0.318228     2.183000E-03
WILS 0.0            0.0
EQUA BR2CLMECARBSOL=CARBSOL+BR2CLMEAQ
```

In this example:
Medium: CARBSOL
Chemical species interaction pair names: CARBSOL and BR2CLMECARBSOL
Molecular weight of HION + Medium: 4376
Equilibrium constant: -5.55641
Margules model parameters: -1.44203, 0.318228 and 2.183000E-03
Equilibrium equation:

Br2CLME + CARBONSOL = Br2CLMECARBSOL

Molecular adsorption species database entries are located in the Species chapter. Below are the entries of CARBSOL and BR2CLMECARBSOL.

```
**BASE LEVEL  0
NAME CARBSOL
**GENE LEVEL  1
DATE 04/15/2008
CHEM CARBSOL
MOLW 204.399994
MATC 8001    0      0      0      0      0      0      0      0      0
STOI 1       0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
+    0.0
**SOLI LEVEL  1
DATE 04/15/2008
HREF -2.720540E+08
VREF 7.220000E-04
CPRE 764804

**BASE LEVEL  0
NAME BR2CLMECARBSOL
**GENE LEVEL  1
DATE 04/15/2008
CHEM BR2CLMECARBSOL
MOLW 412.679993
MATC 2222    8001   0      0      0      0      0      0      0      0
STOI 1       1      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
**SOLI LEVEL  1
DATE 04/15/2008
HREF -3.006900E+08
VREF 7.220000E-04
CPRE 764804
```

Chapter 4 Adsorption Examples

Ion exchange

ProChem is used in this example to study ion exchange between Clinoptilolite and NaCl/KCl mixture at 25 ^{0}C. Ion exchange reaction is represented as follows:

$$K^{+} + NaCLINOPTSOL \leftrightarrow Na^{+} + KCLINOPTSOL$$

MSE thermodynamics model is used to calculate activity coefficient for aqueous solution and Wilson's model for solid phase. Below is the chemistry model. Notice that in the head of MOD file, EXCHWI represents Wilson's model.

Chemistry model

```
ESP EXCHWI MULTEQ2 FRAME EDAT TERM DISK
;
;     *** INPUT      ****
;
INPUT
H2OIN          INFL
KCLIN          INFL
NACLIN          INFL
NACLINOPTSOLIN   INFL
HCLIN
KOHIN
HCL.1H2OIN
HCL.2H2OIN
HCL.3H2OIN
KOH.1H2OIN
KOH.2H2OIN
KOH.4H2OIN
NACL.2H2OIN
NAOH.1H2OIN
NAOH.2H2OIN
NAOH.3.5H2OIN
NAOH.4H2OIN
NAOH.5H2OIN
NAOH.7H2OIN
NAOHIN
K2OIN
NA2OIN
KCLINOPTSOLIN
;
;              *** SPECIES ****
;
SPECIES
H2OVAP
HCLVAP
H2O
HCLAQ
```

```
KOHAQ
CLION
H3OION
KION
NAION
OHION
H2OPPT
KCLPPT
KOHPPT
NACLPPT
NAOHPPT
HCL.1H2O
HCL.2H2O
HCL.3H2O
KOH.1H2O
KOH.2H2O
KOH.4H2O
NACL.2H2O
NAOH.1H2O
NAOH.2H2O
NAOH.3.5H2O
NAOH.4H2O
NAOH.5H2O
NAOH.7H2O
KCLINOPTSOL
NACLINOPTSOL
;
;           *** SOLID SCALING TENDENCY ****
;
SOLIDS
ALL
;
;     *** EQUILIBRIUM EQUATIONS ****
;
EQUILIBRIUM
2H2O=H3OION+OHION
H2OPPT=H2O
H2OVAP=H2O
HCL.1H2O=HCLAQ+H2O
HCL.2H2O=HCLAQ+2H2O
HCL.3H2O=HCLAQ+3H2O
HCLAQ+H2O=H3OION+CLION
HCLVAP=HCLAQ
KCLPPT=KION+CLION
KOH.1H2O=KION+OHION+1H2O
KOH.2H2O=KION+OHION+2H2O
KOH.4H2O=KION+OHION+4H2O
KOHAQ=KION+OHION
KOHPPT=KION+OHION
NACL.2H2O=NAION+CLION+2H2O
NACLPPT=NAION+CLION
NAOH.1H2O=NAION+OHION+H2O
NAOH.2H2O=NAION+OHION+2H2O
NAOH.3.5H2O=NAION+OHION+3.5H2O
NAOH.4H2O=NAION+OHION+4H2O
NAOH.5H2O=NAION+OHION+5H2O
```

```
NAOH.7H2O=NAION+OHION+7H2O
NAOHPPT=NAION+OHION
;
;     *** EXCHANGE    ****
;
EXCHANGE
NACLINOPTSOL+KION=KCLINOPTSOL+NAION
END
```

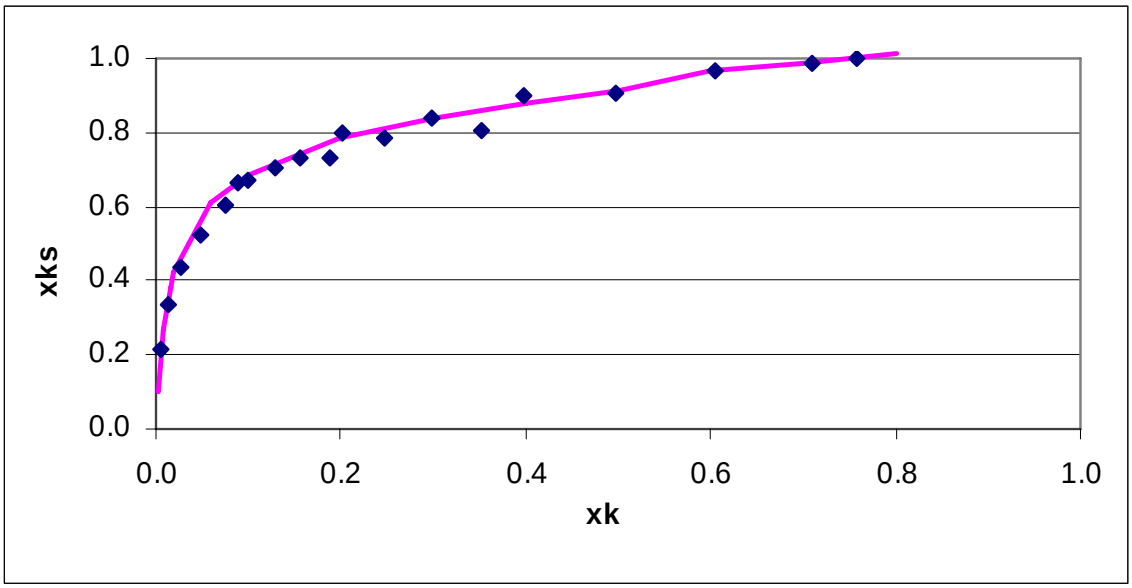
Survey input file

In this example, NACLINOPTSOL concentration is 0.5 gmol/kg H_2O

```
ELEC DISK TERM SRK SOLID
UNITIN HOURS CENTIGRADE ATMOSPHERES GMOLES CALORIES
UNITOUT HOURS CENTIGRADE ATMOSPHERES GMOLES CALORIES
TEMPERATURE     25.00000
PRESSURE        1.00000
H2OIN          55.50868
KCLIN        0.4000E-01 FREE
NACLIN        4.60000E-01 FREE
NACLINOPTIN     5.00000E-01
KION          1.79E-05 FIX
NAION          8.91E-03 FIX
END
KCLIN        0.2000E-01 FREE
NACLIN        4.80000E-01 FREE
NACLINOPTIN     5.00000E-01
KION          7.14E-05 FIX
NAION          8.86E-03 FIX
END
KCLIN        0.2000E-01 FREE
NACLIN        4.80000E-01 FREE
NACLINOPTIN     5.00000E-01
KION          1.43E-04 FIX
NAION          8.78E-03 FIX
END
KCLIN        0.2000E-01 FREE
NACLIN        4.80000E-01 FREE
NACLINOPTIN     5.00000E-01
KION          1.79E-04 FIX
NAION          8.75E-03 FIX
END
KCLIN        0.4000E-01 FREE
NACLIN        4.60000E-01 FREE
NACLINOPTIN     5.00000E-01
KION          5.36E-04 FIX
NAION          8.39E-03 FIX
END
KCLIN        0.5000E-01 FREE
NACLIN        4.50000E-01 FREE
NACLINOPTIN     5.00000E-01
KION          8.93E-04 FIX
NAION          8.03E-03 FIX
END
```

KCLIN 2.0000E-01 FREE
NACLIN 3.00000E-01 FREE
NACLINOPTIN 4.50000E-01
KION 1.79E-03 FIX
NAION 7.14E-03 FIX
END
KCLIN 2.5000E-01 FREE
NACLIN 2.50000E-01 FREE
NACLINOPTIN 4.00000E-01
KION 2.68E-03 FIX
NAION 6.25E-03 FIX
END
KCLIN 3.0000E-01 FREE
NACLIN 2.00000E-01 FREE
NACLINOPTIN 3.00000E-01
KION 3.57E-03 FIX
NAION 5.36E-03 FIX
END
KCLIN 3.5000E-01 FREE
NACLIN 1.50000E-01 FREE
NACLINOPTIN 2.00000E-01
KION 4.46E-03 FIX
NAION 4.46E-03 FIX
END
KCLIN 4.0000E-01 FREE
NACLIN 1.00000E-01 FREE
NACLINOPTIN 1.00000E-01
KION 5.36E-03 FIX
NAION 3.57E-03 FIX
END
KCLIN 4.5000E-01 FREE
NACLIN 0.50000E-01 FREE
NACLINOPTIN 1.00000E-01
KION 6.25E-03 FIX
NAION 2.68E-03 FIX
END
KCLIN 4.0000E-01 FREE
NACLIN 1.00000E-01 FREE
NACLINOPTIN 1.00000E-01
KION 7.14E-03 FIX
NAION 1.79E-03 FIX
END
KCLIN 4.9000E-01 FREE
NACLIN 0.10000E-01 FREE
NACLINOPTIN 0.40000E-01
KION 8.03E-03 FIX
NAION 8.93E-04 FIX
END

Results



Uptake plot calculation for the Na+/K+ exchange. Experimental data is from Pabalan, T. R., “thermodynamics of Ion Exchange between Clinoptilolite and Aqueous Solutions of Na+/K+ and Na+/Ca2+”, *Geochimica et Cosmochimica Acta*, 58, 4573-4590, (1990)

Surface complexation

Surface acidity equilibrium

All equations and constants are taken from the book of Dzombak & Morel.

Table 2.1 Surface Acidity (page 17)

Table 5.7 Best Estimates for HFO Acidity Constants (page 101)

$\equiv Fe^{s}\text{-}O\text{-}H_2^{+}$	$\Leftrightarrow$	H^{+}	+	$\equiv Fe^{s}\text{-}O\text{-}H^{o}$	$\log K_{a1\text{-}s}^{int} = -7.29$
H2OHFO1CPI	=	HION	+	HOHFO1CPM	
$\equiv Fe^{w}\text{-}O\text{-}H_2^{+}$	$\Leftrightarrow$	H^{+}	+	$\equiv Fe^{w}\text{-}O\text{-}H^{o}$	$\log K_{a1\text{-}w}^{int} = -7.29$
H2OHFO2CPI	=	HION	+	HOHFO2CPM	
$\equiv Fe^{s}\text{-}O\text{-}H^{o}$	$\Leftrightarrow$	H^{+}	+	$\equiv Fe^{s}\text{-}O^{-}$	$\log K_{a2\text{-}s}^{int} = -8.93$
HOHFO1CPM	=	HION	+	OHFO1CPI	
$\equiv Fe^{w}\text{-}O\text{-}H^{o}$	$\Leftrightarrow$	H^{+}	+	$\equiv Fe^{w}\text{-}O^{-}$	$\log K_{a2\text{-}w}^{int} = -8.93$
HOHFO2CPM	=	HION	+	OHFO2CPI	

Based upon Dzombak & Morel, *Figure IT7*, page 99

HFO density: 1.4 gm/liter (specified in Figure IT7)
HFO Site 2 Site Density: 0.2 gmole/gmole solid
HFO Molecular Weight ($\equiv Fe^{S}\text{-}O^{-}$): 87.8458

Thus, HFO "Feed":

$$\text{HFO (gmole ads surf/liter)} = \frac{1.4 \text{ gm HFO/liter} * .2 \text{ gmole ads surf/gmole HFO}}{87.8458 \text{ gm HFO/gmole HFO}}$$

$$= 0.003187 \text{ gmole ads surf/liter}$$

HFO1 = (.005/.205) * HFO = 7.878E-05 gmole
HFO2 = (.200/.205) * HFO = 0.003151 gmole

To determine pH as a function of OH^{-}/H^{+} added, vary KOHIN and HCLIN

Chemistry model

Here is the chemistry model (.MOD) of surface acidity case

```
ESP FRAME EDAT TERM DISK SCDLM
;
;     *** INPUT      ****
;
INPUT
H2OIN          INFL
NANO3IN        INFL
KNO3IN         INFL
NAOHIN         INFL
HCLIN          INFL
HOHFO1CPMIN    INFL
HOHFO2CPMIN    INFL
HNO3IN
KCLIN
KOH.1H2OIN
KOH.2H2OIN
KOHIN
NACLIN
NAOH.1H2OIN
H2OHFO1CPIIN
H2OHFO2CPIIN
OHFO1CPIIN
OHFO2CPIIN
K2OIN
N2O5IN
NA2NO3OHIN
NA2OIN
NA3NO3OH2IN
NAKNO32IN
;
;              *** SPECIES ****
;
SPECIES
H2OVAP
HCLVAP
HNO3VAP
H2O
HCLAQ
HNO3AQ
HOHFO1CPM
HOHFO2CPM
KCLAQ
NANO3AQ
CLION
H2OHFO1CPI
H2OHFO2CPI
HION
KION
NAION
NO3ION
OHFO1CPI
OHFO2CPI
```

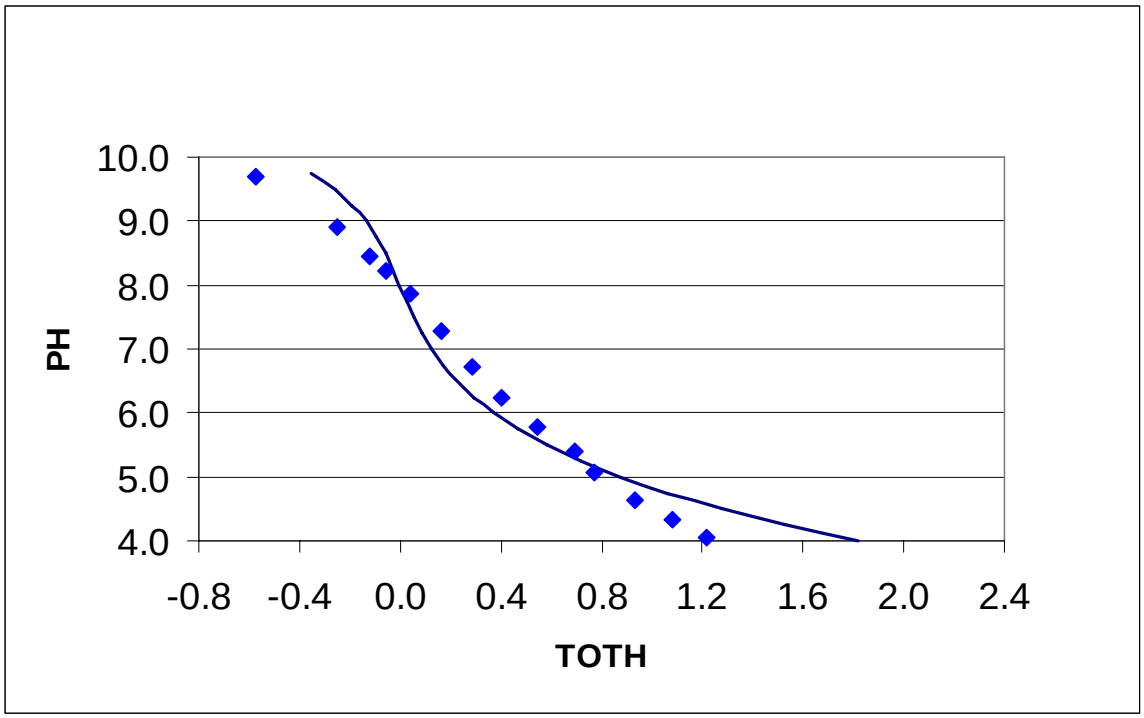
```
OHION
KCLPPT
KNO3PPT
KOHPPT
NACLPPT
NANO3PPT
NAOHPPT
KOH.1H2O
KOH.2H2O
NAOH.1H2O
;
;          *** SOLID SCALING TENDENCY ****
;
SOLIDS
ALL
;
;     *** EQUILIBRIUM EQUATIONS ****
;
EQUILIBRIUM
H2O=HION+OHION
H2OVAP=H2O
HCLAQ=HION+CLION
HCLVAP=HCLAQ
HNO3AQ=HION+NO3ION
HNO3VAP=HNO3AQ
KCLAQ=KION+CLION
KCLPPT=KION+CLION
KNO3PPT=KION+NO3ION
KOH.1H2O=KION+OHION+1H2O
KOH.2H2O=KION+OHION+2H2O
KOHPPT=KION+OHION
NACLPPT=NAION+CLION
NANO3AQ=NAION+NO3ION
NANO3PPT=NAION+NO3ION
NAOH.1H2O=NAION+OHION+H2O
NAOHPPT=NAION+OHION
;
;     *** EQUATIONS   ****
;
EQUATIONS
DEFINE MH=EXP(LHION)*LIQMOL
DEFINE MOH=EXP(LOHION)*LIQMOL
DEFINE MHFO1=EXP(LH2OHFO1CPI)*LIQMOL
DEFINE MHFO2=EXP(LH2OHFO2CPI)*LIQMOL
DEFINE MOFO1=EXP(LOHFO1CPI)*LIQMOL
DEFINE MOFO2=EXP(LOHFO2CPI)*LIQMOL
DEFINE TOTHUSE=(MH-MOH+MHFO1-MOFO1+MHFO2-MOFO2)*1000.0
;
;     *** COMPLEXATION****
;
COMPLEXATION
H2OHFO1CPI=HION+HOHFO1CPM
H2OHFO2CPI=HION+HOHFO2CPM
HOHFO1CPM=HION+OHFO1CPI
HOHFO2CPM=HION+OHFO2CPI
END
```

ProChem input file (.INP)

```
ELEC DISK TERM SRK SOLID
UNITIN HOURS CENTIGRADE ATMOSPHERES GMOLES CALORIES
UNITOUT HOURS CENTIGRADE ATMOSPHERES GMOLES CALORIES
TEMPERATURE      25.00000
PRESSURE         1.00000
H2OIN           55.50868
KNO3IN           0.010
KOHIN           4.00000E-04
HOHFO2IN         3.18700E-03
HOHFO1IN         7.96850E-05
HCLIN           1.0E-4     FREE
PRINT OHION HION H2OHFO1CPI H2OHFO2CPI OHFO1CPI OHFO2CPI TOTHUSE
PH              4.00 INCR 0.25 REPE 23 FIX
END
```

Surface acidity case results

PT.	TOTHUSE	PH
1	1.81793	4.00000
2	1.52549	4.25000
3	1.27500	4.50000
4	1.05975	4.75000
5	0.874902	5.00000
6	0.716642	5.25000
7	0.581760	5.50000
8	0.467492	5.75000
9	0.371391	6.00000
10	0.291204	6.25000
11	0.224774	6.50000
12	0.169976	6.75000
13	0.124706	7.00000
14	8.689421E-02	7.25000
15	5.452987E-02	7.50000
16	2.565876E-02	7.75000
17	-1.641159E-03	8.00000
18	-2.931936E-02	8.25000
19	-5.944648E-02	8.50000
20	-9.435053E-02	8.75000
21	-0.136819	9.00000
22	-0.190419	9.25000
23	-0.260041	9.50000
24	-0.352873	9.75000



HFO. 1.4 g.L and I = 0.01 M KNO_3, HCl is used to vary pH. Experimental data from figure 1T7 of Dzombak and Morel book.

If surface complexation results are displayed as 'Molecular Composition' or 'Molecular Phase', there are some solid species which cannot be found in MOD files or DBS file, and are "faked" solid species. The reason they are displayed is that inside OLI SOLVER, surface complexation reactions generate CPI species, which are ions but are not affiliated to any corresponding molecule species. If it is worked on true species base, those ionic species are viewed as what they are. However, if it is worked on the base of molecule such as streams in a flowsheet, those CPI species have to convert to solids. Those solid species may be treated as pseudo solids, by combining CPI species with ions available in the system under the condition of electrolytic neutrality.

VO4/HFO adsorption case:

Chemistry model

```
ESP FRAME EDAT TERM DISK SCDLM
;
;
;            *** INFLOWS ***
;
INPUT
H2OIN          INFL
NANO3IN        INFL
```

```
NAOHIN          INFL
HOHFO1CPMIN     INFL
HOHFO2CPMIN     INFL
NA3VO4IN        INFL
HCLIN           INFL
H2OHFO1CPIIN
H2OHFO2CPIIN
OHFO1CPIIN
OHFO2CPIIN
H3VO4IN
HNO3IN
N2O5IN
NA2NO3OHIN
NA2OIN
NA3NO3OH2IN
NACLIN
NAOH.1H2OIN
NAVO3IN
V2O5IN
VO2CLIN
VO2OHIN
VOOH3IN
HOVO4HFO1CPIIN
HOVO4HFO2CPIIN
;
;              *** SPECIES ***
;
SPECIES
;
;               - VAPORS -
H2OVAP
HCLVAP
HNO3VAP
;
;               - AQUEOUS -
H2O
H3VO4AQ
HCLAQ
HNO3AQ
HOHFO1CPM
HOHFO2CPM
NANO3AQ
VO2CLAQ
;
;                - IONS -
CLION
H2OHFO1CPI
H2OHFO2CPI
H2VO4ION
HION
HOVO4HFO1CPI
HOVO4HFO2CPI
HVO4ION
NAION
NO3ION
OHFO1CPI
```

```
OHFO2CPI
OHION
VO2ION
VO4ION
;
;            - PRECIPITATES -
NA3VO4PPT
NACLPPT
NANO3PPT
NAOHPPT
NAVO3PPT
VO2CLPPT
;
;              - HYDRATES -
NAOH.1H2O
;
;              - SUSPEND SOLIDS -
;
SOLIDS
ALL
;
;    ***EQUILIBRIUM EQUATIONS***
;
EQUILIBRIUM
H2O=HION+OHION
H2OVAP=H2O
H2VO4ION=HION+HVO4ION
H3VO4AQ=H2VO4ION+HION
HCLAQ=HION+CLION
HCLVAP=HCLAQ
HNO3AQ=HION+NO3ION
HNO3VAP=HNO3AQ
HVO4ION=HION+VO4ION
NA3VO4PPT+2HION=3NAION+H2VO4ION
NACLPPT=NAION+CLION
NANO3AQ=NAION+NO3ION
NANO3PPT=NAION+NO3ION
NAOH.1H2O=NAION+OHION+H2O
NAOHPPT=NAION+OHION
NAVO3PPT+H2O=NAION+H2VO4ION
VO2CLAQ=VO2ION+CLION
VO2CLPPT=VO2ION+CLION
VO2ION+2H2O=H2VO4ION+2HION
;
;      *** COMPLEXATION ***
;
COMPLEXATION
H2OHFO1CPI=HION+HOHFO1CPM
H2OHFO2CPI=HION+HOHFO2CPM
HOHFO1CPM=HION+OHFO1CPI
HOHFO2CPM=HION+OHFO2CPI
HOVO4HFO1CPI+HION=HOHFO1CPM+HVO4ION
HOVO4HFO2CPI+HION=HOHFO2CPM+HVO4ION
;
;     *** EQUATIONS   ****
;
```

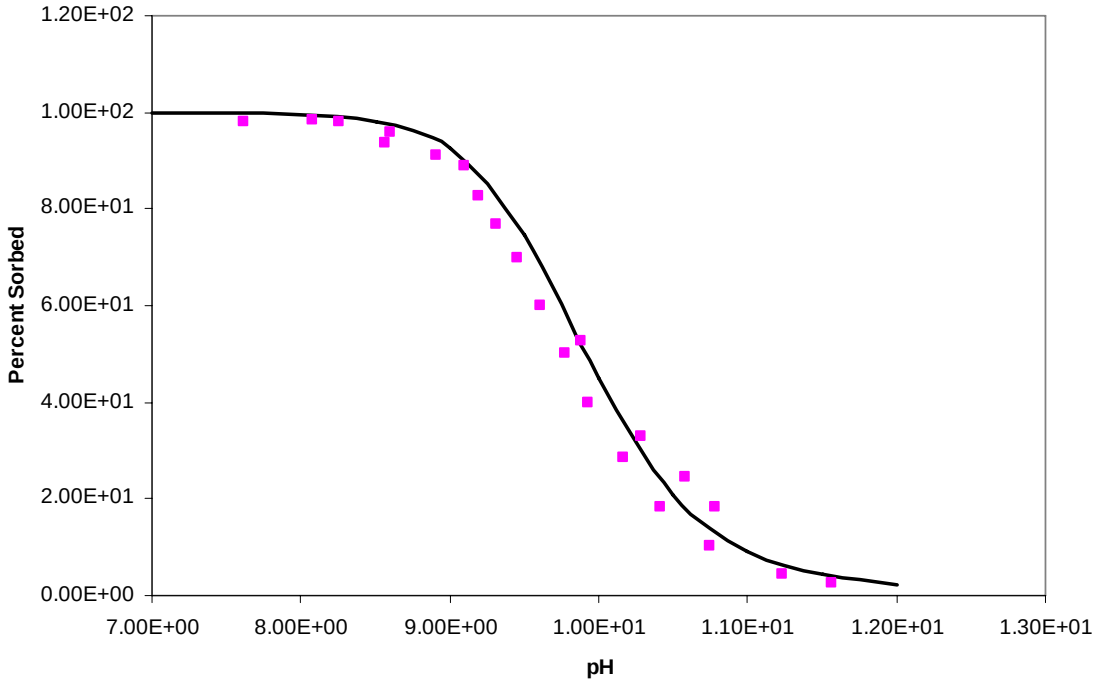
```
EQUATIONS
DEFINE MHOV1=EXP(LHOVO4HFO1CPI)*LIQMOL
DEFINE MHOV2=EXP(LHOVO4HFO2CPI)*LIQMOL
DEFINE MTOT=(MHOV1+MHOV2)
DEFINE PERADS=MTOT/NA3VO4IN*100
;
END
```

Input file

```
ELEC DISK TERM SRK SOLID
UNITIN HOURS CENTIGRADE ATMOSPHERES GMOLES CALORIES
UNITOUT HOURS CENTIGRADE ATMOSPHERES GMOLES CALORIES
TEMPERATURE     25.00000
PRESSURE        1.00000
H2OIN          55.50868
NANO3IN         1.00000E-01
NA3VO4IN        1.0000E-07
HOHFO2IN         4.00E-05
HOHFO1IN         1.00E-06
HCLIN          1.00E-3
NAOHIN          1.00000E-05  FREE
PH        7.000 INCR 0.5 REPE 10 FIX
END
```

Results

PT.	PH	PERADS
1	7.00000	99.9270
2	7.50000	99.8561
3	8.00000	99.5635
4	8.50000	98.2109
5	9.00000	92.3830
6	9.50000	74.4735
7	10.0000	44.9447
8	10.5000	20.9780
9	11.0000	9.07261
10	11.5000	4.20751
11	12.0000	2.27661



TOTFe = 2.00E-4 M, TOTVO4 = 1.00E-7 M. Experimental data from Figure 1EVA1 of Dzombak and Morel book.

Molecular adsorption

Carbon adsorption of chlorodibromomethane (OLI name BR2CLME)
Generate a curve of adsorbed cholorodibromomethane and concentration in solution to compare with experimental and an ideal solid (Langmuir) model.

Chemistry model

Chemistry model file (*.MOD) includes EXCHANGE section which defines the molecular adsorption interaction and EQUATION section which adds ALG and DEFINE variables.

```
ESP FRAME EDAT TERM DISK
;
;
;             *** INFLOWS ***
;
INPUT
H2OIN          INFL
BR2CLMEIN      INFL
CARBSOLIN      INFL
BR2CLMECARBSOLIN INFL
;
;             *** SPECIES ***
;
SPECIES
;
;              - VAPORS -
BR2CLMEVAP
H2OVAP
;
;              - AQUEOUS -
H2O
BR2CLMEAQ
;
;               - IONS -
HION
OHION
;
;            - PRECIPITATES -
;
;              - HYDRATES -
;
;              - SUSPEND SOLIDS -
;
;             - ION EXCHANGE SOLIDS -
BR2CLMECARBSOL
CARBSOL
SOLIDS
ALL
;
;   ***EQUILIBRIUM EQUATIONS***
;
```

```
EQUILIBRIUM
BR2CLMEVAP=BR2CLMEAQ
H2O=HION+OHION
H2OVAP=H2O
;
;      *** ION EXCHANGE ***
;
EXCHANGE
BR2CLMECARBSOL=BR2CLMEAQ+CARBSOL
;
EQUATIONS
ALG CONC=(BR2CLMEAQ*LIQMOL)/VOLLIQ
DEFINE CQ=BR2CLMEAQ/H2O/0.018
END
```

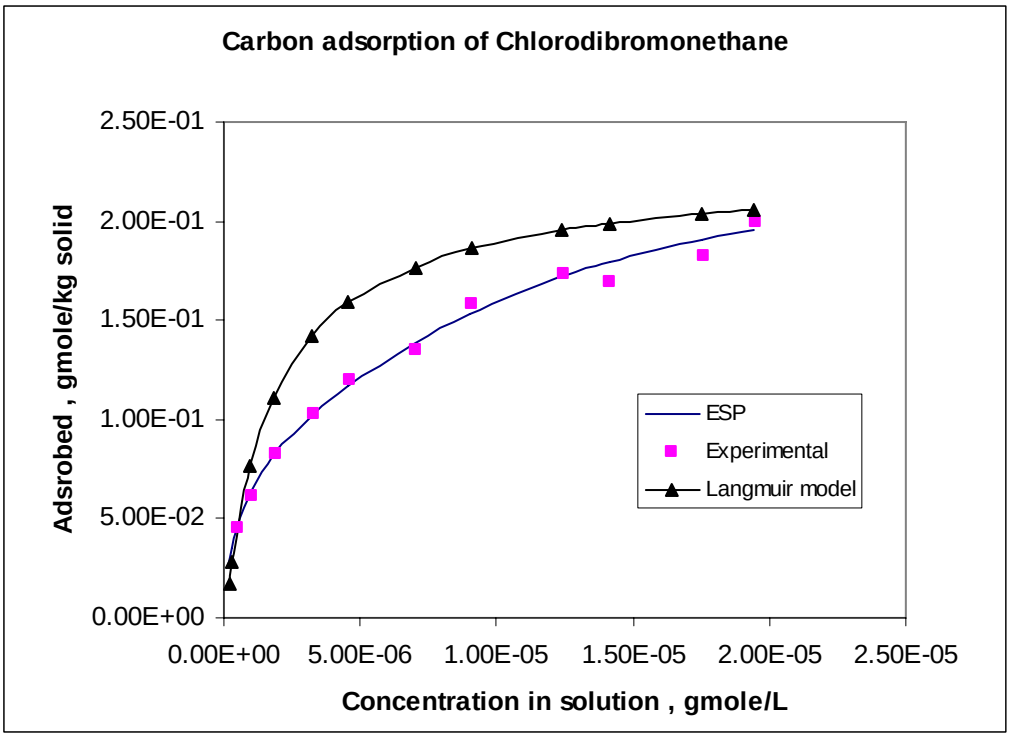
ProChem input file (*.inp)

```
ELEC DISK TERM SRK
UNITIN HOURS CENTIGRADE ATMOSPHERES GMOLES CALORIES
UNITOUT HOURS CENTIGRADE ATMOSPHERES GMOLES CALORIES
TEMPERATURE     25.00000
PRESSURE        1.00000
H2OIN          55.50810
BR2CLMEIN       9.88419E-07 FREE
CARBIN          1.00000
CONC           1.65640E-07 FIX
PRINT BR2CLMEAQ BR2CLMECARBSOL BR2CLMEIN SOLMAS CONC CQ
END
CONC          2.86150E-07  FIX
END
CONC          4.94530E-07  FIX
END
CONC          1.01310E-06  FIX
END
CONC          1.85810E-06  FIX
END
CONC          3.26480E-06  FIX
END
CONC          4.53240E-06  FIX
END
CONC          6.98100E-06  FIX
END
CONC          9.04550E-06  FIX
END
CONC          1.24110E-05  FIX
END
CONC          1.41300E-05  FIX
END
CONC          1.75340E-05  FIX
END
CONC          1.93920E-05  FIX
END
```

Results for variable of interest (PRT file)

Solid phase concentration BR2CLMECARBSOL (gmole chlorodibromomethane/kg Solid)

PT	CONC	BR2CLMECARBS
1	1.656400E-07	2.628221E-02
2	2.861500E-07	3.547617E-02
3	4.945300E-07	4.650330E-02
4	1.013100E-06	6.405029E-02
5	1.858100E-06	8.219237E-02
6	3.264800E-06	0.102636
7	4.532400E-06	0.116646
8	6.981000E-06	0.138175
9	9.045500E-06	0.152931
10	1.241100E-05	0.172009
11	1.413000E-05	0.179567
12	1.753400E-05	0.190819
13	1.939200E-05	0.195315



Carbon adsorption of chlorodibromomethane

Comparison is made between Langmuir model, OLI model and experimental data. Experimental data from a plot published in “Prediction of Fixed-Bed Adsorber Removal of Organics in Unknown Mixtures” Crittendon, Luft and Hand, Journal of Environmental Engineering, Vol 113, No. 3, June, 1987

Chapter 5 regression

Ion exchange

This example is created to demonstrate the development of two parameters of Wilson's model and equilibrium constant using uptake experimental data.
Here is the input file of OLI's standalone regression program, *.INR file.

Input

```
$TITLE
  K, Na ION Exchange
;
$CONTROL
 MAXIT 1000
 METH 2
 MARQ 100.
 ERROR 1
 OBJECT 2
;
$PARAMETERS
   P01 1.0       1.471   1.5     1.95    KNACLINOPTSOL  A
   P02 1.0       2.226   0.0     0.10    NACLINOPTSOL KCLINOPTSOL  WILIJ
   P03 1.0       1.323   0.0     0.10    NACLINOPTSOL KCLINOPTSOL  WILJI
;
$DATA SET 1
TEMPERATURE      25.00000
PRESSURE         1.00000
H2OIN            55.50868
DATA NACLINOPTIN    KCLIN    NACLIN   :   KION     NAION
0.500000    0.051584    0.453000       0.000018    0.008909
0.500000    0.137140    0.367650       0.000071    0.008856
0.500000    0.197720    0.306600       0.000143    0.008784
0.500000    0.218800    0.285870       0.000179    0.008749
0.500000    0.330180    0.174350       0.000536    0.008392
0.500000    0.389150    0.115240       0.000893    0.008034
0.450000    0.449360    0.055517       0.001785    0.007142
0.400000    0.481900    0.023060       0.002678    0.006249
0.300000    0.460620    0.044425       0.003571    0.005356
0.200000    0.430550    0.074001       0.004464    0.004464
0.100000    0.394900    0.110320       0.005356    0.003571
0.100000    0.447450    0.057847       0.006249    0.002678
0.100000    0.499890    0.005491       0.007142    0.001785
END
```

Results of the regression (NRM file)

Here is the output file of the regression, *.NRM file in which the final values the regressed parameters are

```
1.415D+00  8.359D-01  2.982D+00
DATA SET   1
PTS Dep Variable        Exper       Calculated   Obj Function
  1 KION            1.80000E-05  1.79492E-05     -0.00283      0 L1
  1 NAION           8.90900E-03  8.90989E-03      0.00010      0 L1
  2 KION            7.10000E-05  7.14210E-05      0.00593      0 L1
  2 NAION           8.85600E-03  8.85991E-03      0.00044      0 L1
  3 KION            1.43000E-04  1.42852E-04     -0.00104      0 L1
  3 NAION           8.78400E-03  8.78019E-03     -0.00043      0 L1
  4 KION            1.79000E-04  1.78767E-04     -0.00130      0 L1
  4 NAION           8.74900E-03  8.75030E-03      0.00015      0 L1
  5 KION            5.36000E-04  5.35114E-04     -0.00166      0 L1
  5 NAION           8.39200E-03  8.39092E-03     -0.00013      0 L1
  6 KION            8.93000E-04  8.92003E-04     -0.00112      0 L1
  6 NAION           8.03400E-03  8.03101E-03     -0.00037      0 L1
  7 KION            1.78500E-03  1.78980E-03      0.00269      0 L1
  7 NAION           7.14200E-03  7.14018E-03     -0.00026      0 L1
  8 KION            2.67800E-03  2.68063E-03      0.00098      0 L1
  8 NAION           6.24900E-03  6.24931E-03      0.00005      0 L1
  9 KION            3.57100E-03  3.57105E-03      0.00001      0 L1
  9 NAION           5.35600E-03  5.35891E-03      0.00054      0 L1
 10 KION            4.46400E-03  4.46098E-03     -0.00068      0 L1
 10 NAION           4.46400E-03  4.45894E-03     -0.00113      0 L1
 11 KION            5.35600E-03  5.36062E-03      0.00086      0 L1
 11 NAION           3.57100E-03  3.56945E-03     -0.00043      0 L1
 12 KION            6.24900E-03  6.25063E-03      0.00026      0 L1
 12 NAION           2.67800E-03  2.67935E-03      0.00050      0 L1
 13 KION            7.14200E-03  7.14060E-03     -0.00020      0 L1
 13 NAION           1.78500E-03  1.78940E-03      0.00246      0 L1

 DATA SET   1 NORM IS =  6.817308E-05


 Parm      Value       d(objective)/d(parm)     (Change Objective)/(1% change in parm)

 P01     1.415377      -11.67768               -0.1652832
 P02    0.8358675      -1.300751               -1.0872553E-02
 P03     2.982049     -0.8139127               -2.4271278E-02


 ITERATION=   22    NORM FOR CONV PTS= 6.817308E-05

 Mean value= 1.31299E-04   Std Dev= 1.645902E-03
```

Surface complexation

Magnetite acidity titration regression case:

Input

```
$TITLE
MAGNETITE  ACIDITY TRITATION
;
$CONTROL
MAXIT 10000
METH 2
MARQ 1000.
SCALE 1.2
ERROR 1
OBJECT 2
FULLPRINT
TRACE
;NUMERICAL
CSV PH MPOT1 MPOT PERADS
;
$PARAMETERS
  P01 1  -1.0330    1.5     1.95      KH2OFEO2CPI A
  P02 1  -11.20    0.0     0.10     KHOFEO2CPM  A
  P03 0   7.415     0.0     0.10      KH2BO3FEO2CPM  A
  P04 0  1.2660 0.0     0.10      KBOH3OFEO2CPI   A
  P05 0  1.2770 0.0     0.10       HOBOH4FEO2CPI A
;
$DATA SET 1
TEMPERATURE      25.00000
PRESSURE         1.00000
H2OIN           55.50868
KCLIN           1.00000E-4
HOFEO2IN         5.260E-04
FREE HCLIN      0.0001
FIX PH
DATA HCLIN PH    :  MPOT1
;0.001   4.20E+00   2.61E+01
0.001   4.98E+00   2.78E+01
0.001   5.18E+00   2.42E+01
0.001   6.01E+00   6.14E+00
0.001   6.80E+00   -4.47E+00
$DATA SET 1
TEMPERATURE      25.00000
PRESSURE         1.00000
H2OIN           55.50868
KCLIN           1.00000E-4
HOFEO2IN         5.260E-04
FREE KOHIN       0.0001
FIX PH
DATA KOHIN PH    :  MPOT1
0.0001   7.26E+00   -9.25E+00
0.0001   7.82E+00   -1.67E+01
0.0001   8.06E+00   -2.30E+01
```

```
0.0001   8.84E+00   -3.36E+01
END
```

Results of the regression (NRM file)

```
-1.033D+00 -1.200D+01  7.415D+00  1.266D+00  1.277D+00
DATA SET   1
PTS Dep Variable       Exper       Calculated   Obj Function
  1 MPOT1             27.800      22.361        -0.24321       0 L1
  2 MPOT1             24.200      19.476        -0.24253       0 L1
  3 MPOT1             6.1400      7.3653         0.19956       0 L1
  4 MPOT1            -4.4700     -4.0951        -0.09155       0 L1

 DATA SET   1 NORM IS =  0.166178

DATA SET   2
PTS Dep Variable       Exper       Calculated   Obj Function
  5 MPOT1            -9.2500     -10.813         0.16898       0 L1
  6 MPOT1            -16.700     -19.100         0.14369       0 L1
  7 MPOT1            -23.000     -22.679        -0.01418       0 L1
  8 MPOT1            -33.600     -34.273         0.02002       0 L1

 DATA SET   2 NORM IS =  4.980125E-02


 Parm      Value       d(objective)/d(parm)     (Change Objective)/(1% change in parm)

 P01    -1.033385      -1.289223               1.3322637E-02
 P02    -12.00192       4.608904              -0.5531571
 P03     7.415000        0.0000000              0.0000000
 P04     1.266000        0.0000000              0.0000000
 P05     1.277000        0.0000000              0.0000000


 ITERATION=   62    NORM FOR CONV PTS= 0.215979

 Mean value= -7.40300E-03    Std Dev= 0.175475
```

Molecular adsorption

Carbon adsorption of chlorodibromomethane (OLI name BR2CLME)
In this example, equilibrium constant K, three Margul's parameters are obtained by fitting to experimental data. Notice that the chemistry model is different than that in Chapter 4. Here the variable CONC is defined as DEFINE variable, rather than ALG variable as defined in the chemistry model of Chapter 4.

Input

```
$TITLE
  Carb, BR2CLME molecular adsorption
;
$CONTROL
 MAXIT 100
 METH 2
 MARQ 100.
 ERROR 1
 OBJECT 2
;
$PARAMETERS
   P01 1       -7.55641   1.5     1.95    KBR2CLMECARBSOL    A
   P02 1       -3.44203   0.0     0.10    BR2CLMECARBSOL CARBSOL  AIJ
   P03 1        0.318228  0.0     0.10    BR2CLMECARBSOL CARBSOL  AJI
   P04 1        0.002183  0.0     0.10    BR2CLMECARBSOL CARBSOL DIJ
;
$DATA SET 1
TEMPERATURE      25.00000
PRESSURE         1.00000
H2OIN           55.50868
CARBIN           1.00
DATA BR2CLMEIN : CONC
1.150111E-01     1.66E-07
1.552440E-01     2.86E-07
2.034989E-01     4.95E-07
2.802851E-01     1.01E-06
3.596757E-01     1.86E-06
4.491379E-01     3.26E-06
5.104454E-01     4.53E-06
6.046619E-01     6.98E-06
6.692359E-01     9.05E-06
7.527221E-01     1.24E-05
7.858008E-01     1.41E-05
8.350407E-01     1.75E-05
8.547188E-01     1.94E-05
END
```

Results of the regression (NRM file)

-5.557D+00 -1.437D+00 3.221D-01 1.428D-02

DATA SET 1

PTS	Dep Variable	Exper	Calculated	Obj Function	
1	CONC	1.66000E-07	1.65866E-07	-0.00081	0 L1 S
2	CONC	2.86000E-07	2.86322E-07	0.00113	0 L1 S
3	CONC	4.95000E-07	4.94490E-07	-0.00103	0 L1 S
4	CONC	1.01000E-06	1.01236E-06	0.00233	0 L1 S
5	CONC	1.86000E-06	1.85630E-06	-0.00199	0 L1 S
6	CONC	3.26000E-06	3.26194E-06	0.00060	0 L1 S
7	CONC	4.53000E-06	4.52924E-06	-0.00017	0 L1 S
8	CONC	6.98000E-06	6.97810E-06	-0.00027	0 L1 S
9	CONC	9.05000E-06	9.04256E-06	-0.00082	0 L1 S
10	CONC	1.24000E-05	1.24051E-05	0.00041	0 L1 S
11	CONC	1.41000E-05	1.41208E-05	0.00147	0 L1 S
12	CONC	1.75000E-05	1.75152E-05	0.00087	0 L1 S
13	CONC	1.94000E-05	1.93667E-05	-0.00172	0 L1 S

DATA SET 1 NORM IS = 1.956997E-05

Parm	Value	d(objective)/d(parm)	(Change Objective)/(1% change in parm)
P01	-5.556593	29.96578	-1.665077
P02	-1.436944	-0.7794421	1.1200148E-02
P03	0.3220775	0.6287813	2.0251630E-03
P04	1.4279259E-02	0.1148512	1.6399901E-05

ITERATION= 18 NORM FOR CONV PTS= 1.956997E-05

Mean value= -5.66493E-07 Std Dev= 1.277040E-03