

# A BRIEF GUIDE TO USING OLI/MSE DATA REGRESSION

## OLI Systems, Inc.

This manual outlines the use of OLI/MSE regression program with focus on items that are different from using the conventional OLI data regression facility and those that are added specifically for the OLI/MSE framework. The readers need to refer to *A Guide to Using OLI Data Regression* and other related OLI manuals for features of the OLI software and the syntax used.

### I. THE MSE DATABASE (H<sub>3</sub>O<sup>+</sup> version)

A databank has been created for use with the OLI/MSE framework. The databank is called *MSEPUB*, and contains several data items specifically used by the MSE model, in addition to those that already in the other OLI databanks, such as standard state properties (e.g. Gibbs free energy and enthalpy of formation, entropy, and heat capacity), and the Helgeson-Kirkham-Flowers (HKF) equation of state parameters.

#### New data items for *Aqueous Phase*:

LDEN – Coefficients, A, B, C, and D, for pure liquid molar density. The liquid density is calculated based on the following equation:<sup>1</sup>

$$\rho(\text{kmol} / \text{m}^3) = \frac{A}{B^{1+(1-T/C)^D}}$$

DIE0 – Coefficients for the dielectric constant of the pure liquid, calculated based on the following equation:<sup>2</sup>

$$\varepsilon = E + \frac{F}{T}$$

R\_UQ –

Q\_UQ –

UNIQUAC size (R) and surface (Q) parameters, respectively. Default values are 1.0. For inorganic species (ions and neutral molecules), values for water (R=0.92 and Q=1.40) should be entered. For organic species, values can be determined using UNIFAC group contribution method

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<sup>1</sup> Daubert, T. E. and Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals*. Hemisphere Publishing Corporation, New York, 1989

<sup>2</sup> Wang, P. and Anderko A., *Fluid Phase Equilibria*, 186 (2001) 103-122.

discussed by Fredenslund et al. (*AIChE J.* **1975**, 21, 1086-1099). The group specifications and values of the R and Q assignments can be found in references such as *The Properties of Gases and Liquids*, 4<sup>th</sup> Edition (by Reid, R. C.; Prausnitz, J. M.; Poling, B. E. McGraw-Hill Book Company, New York, 1987) and *Vapor-liquid Equilibria using UNIFAC* (by Fredenslund, A.; Gmehling, J. Rasmussen, P. Elsevier, New York, 1977).

CP – Heat capacity parameters for pure liquid. The liquid heat capacity is calculated based on the following equation:<sup>1</sup>

$$C_p(J \cdot mol^{-1} \cdot K^{-1}) = A + BT + CT^2 + DT^3 + ET^4$$

SOLU – Two values are given: solubility of a species (usually organic component) in water and solubility of water in organic.

**Binary interaction parameters in the “INTERACTIONS” chapter:**

UNIQU and EXT-UNIQU – UNIQUAC parameters (primarily for neutral-neutral, can be used for ion-neutral, and ion-ion):

$$a_{ij} = Q0IJ + Q1IJ * T + Q2IJ * T^2 + Q3IJ * T * \ln T + Q4IJ * T^3 + (Q5IJ + Q6IJ * T) * x_i x_j$$

$$a_{ji} = Q0JI + Q1JI * T + Q2JI * T^2 + Q3JI * T * \ln T + Q4JI * T^3 + (Q5JI + Q6JI * T) * x_j x_i$$

$$(a_{ij} \neq a_{ji}; T \text{ in Kelvin})$$

Parameters Q0IJ, Q0JI, Q1IJ, Q1JI, Q2IJ, Q2JI, Q5IJ, Q5JI, Q6IJ, Q6JI are in UNIQU;

Parameters Q3IJ, Q3JI, Q4IJ, Q4JI are in EXT-UNIQU.

For most systems, Q5J, Q6J, Q5I, and Q6I can be set to zero.

MIDRANGE – Middle-range parameters (primarily for neutral-ion and ion-ion; can be used for neutral-neutral):

$$B_{ij} = b_{ij} + c_{ij} \cdot \exp(-\sqrt{I_x + 0.01}) \quad (B_{ij} = B_{ji})$$

$$\text{Where } b_{ij} = BMD0 + BMD1 * T + BMD2 / T + BMD3 * T^2 + BMD4 * \ln T$$

$$c_{ij} = CMD0 + CMD1 * T + CMD2 / T + CMD3 * T^2 + CMD4 * \ln T$$

DENUNIQU – UNIQUAC density parameters:

$$\frac{\partial a_{ij}}{\partial P} = D0IJ + D1IJ * T + D2IJ * T^2$$

$$\frac{\partial a_{ji}}{\partial P} = D0JI + D1JI * T + D2JI * T^2$$

DENMID – Middle-range density parameters:

$$\frac{\partial B_{ij}}{\partial P} = B_{ij}^{(0)} + B_{ij}^{(1)} * \exp\left(-\sqrt{I_X + 0.01}\right) + B_{ij}^{(2)} * P$$

$$\text{Where } B_{ij}^{(0)} = DMD1 + DMD4 * T + DMD5 * T^2$$

$$B_{ij}^{(1)} = DMD2 + DMD3 * T + DMD6 * T^2$$

$$B_{ij}^{(2)} = DMD7 + DMD8 * T + DMD9 * T^2 + DMD0 / T$$

## II. REGRESSION PARAMETERS

The regression parameters that are unique in the MSE framework are those of the UNIQUAC and middle-range parameters. In addition, the MSE framework allows the adjustment of the standard state properties, Gibbs free energy of formation,  $\Delta G_f^0$ , and entropy,  $S^0$ , for both solid and aqueous species, to give better extrapolation behavior of the equilibrium constants with respect to temperature. The standard state parameters such as those of equilibrium constants and HKF equation of state remain to be used if needed. A summary of these parameters is given as follows.

### Standard state parameters –

#### 1. Equilibrium constant parameters (the “KFIT” parameters, A, B, C, D, E, F, G):

The regression parameters and their tag names from the conventional OLI framework remain to be used. However, the MSE framework allows the reference state properties, i.e. Gibbs energy and entropy to be adjusted, which gives better extrapolation behavior for the equilibrium constants with respect to temperature, compared to using these “KFIT” parameters.

#### 2. Standard state Gibbs energy and entropy (appear in the databank as GREF and SREF)

GRFS – standard state Gibbs energy for solid phase

GREF – standard state Gibbs energy for aqueous species

GRFV – standard state Gibbs energy for vapor species

SRFS – standard state entropy for solid phase

SREF – standard state entropy for aqueous species

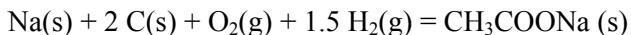
SRFV – standard state entropy for vapor phase species

The adjustment of the standard state Gibbs energy and entropy is the most useful for solid phases with the experimental solubility data and solid heat capacity (if available) as a function of temperature, as the heat capacity of solid influences the temperature dependence of the solubility. The standard state enthalpy can then be calculated from the standard state entropies of the base elements (thermodynamically stable elements) using the well-known thermodynamic relationship.

For example, when GRFS and SRFS for solid sodium acetate (NAACETPPT) are adjusted, its standard state enthalpy ( $\Delta H_f^0$ ) can be automatically calculated based on the standard entropies values of Na(s), C(s), O<sub>2</sub>(g) and H<sub>2</sub>(g). A statement line must be added in the input data file (inr file) before the data set section to give the entropy values for each element and their stoichiometric coefficients in the formation process:

```
ELEM NAACETPPT      1 12.26  2 1.372  1.0 49.0  1.5 31.21
```

The formation process and the standard state entropy for each of the elements are:



12.26 1.372 49.0 31.21 (in cal/mol.K)

Another example (carbamate ion):

```
ELEM NH2CO2ION  1.0  1.372  0.5  45.77  1.0  49.005  1.5  31.21
```

The formation reaction of the carbamate ion and the standard state entropies are:



1.372 45.77 49.005 31.21 0.0

### 3. Heat Capacities:

CPI1, CPI2, CPI3, CPI4, CPI5 – heat capacity equation parameters for vapor species

CPS1, CPS2, CPS3, CPS4, CPS5 – heat capacity equation parameters for solid species

### 4. HKF Equation of state parameters (aqueous species):

a1 = HA1      a2 = HA2      a3 = HA3      a4 = HA4

c1 = HC1      c2 = HC2

$\omega$  = HW

### Excess properties –

Parameters specific for the MSE model are the UNIQUAC and middle-range parameters:

#### 1. UNIQUAC activity coefficient parameters

Q0IJ Q0JI Q1IJ Q1JI Q2IJ Q2JI Q3IJ Q3JI Q4IJ Q4JI

Q5IJ Q5JI Q6IJ Q6JI

#### 2. Middle-range activity coefficient parameters

BMD0 BMD1 BMD2 BMD3 BMD4 CMD0 CMD1 CMD2 CMD3 CMD4

#### 3. UNIQUAC density parameters

D0IJ D0JI D1IJ D1JI D2IJ D2JI

#### 4. Middle-range density parameters

DMD1 DMD2 DMD3 DMD4 DMD5 DMD6 DMD7 DMD8 DMD9 DMD0

### Additional Feature – Constrains in regression parameters

Occasionally, one needs to set one or more interaction parameters to be equal to one or more other parameters in the regression; or to set certain constraints in relation to other parameters. This can be achieved using assignments after the “\$PARAMETERS” section. For example, if parameter 3 and 4 are set equal to parameters 1 and 2 ( $P03=P01$ ,  $P04=P02$ ), and set  $P08=1.5*P06$ ,  $P07=P05+10.0$  in the regression, the assignments can be given following the \$PARAMETERS section:

\$PARAMETERS

```
P01 1 0.1      -1. 1. SPE1  SPE2 BMD0
P02 1 0.001   -1. 1. SPE1  SPE2 BMD1
P03 0 0.      -1. 1. SPE3  SPE4 BMD0
P04 0 0.      -1. 1. SPE3  SPE4 BMD1
P05 1. 32.    -1. 1. SPE5PPT SRFS
P06 1. -40000. -1 1. SPE5PPT GRFS
P07 0 0.      -1. 1. SPE5.H2O SRFS
P08 0. -46000. -1 1. SPE5.H2O GRFS
P03=P01
P04=P02
P08=P06 1.5
P07=P05 1.0 10.0
```

Please note that in this example, the 1<sup>st</sup> column after P03, P04, P07, and P08 must be set to 0.

### III. TYPES OF EXPERIMENTAL DATA AS REGRESSION OBJECTIVES

The types of experimental data that can be used to determine the MSE parameters include not only the excess Gibbs energy/activity data, but also the enthalpy, heat capacity, and density data. The most commonly used data types in regression are:

1. Vapor Pressure (Total pressure, partial pressure, or vapor phase mole fractions)
2. Osmotic coefficients or solvent activities
3. Activity coefficients for completely dissociated aqueous electrolytes
4. Solid solubility
5. Liquid-liquid equilibrium data or mutual solubilities
6. Speciation (e.g. apparent ionization constants in the mixed solvent or concentrations of a particular species in partially dissociated systems)
7. Gibbs energy of transfer of electrolyte from one solvent to another

8. Heat of dilution
9. Heat of mixing
10. Heat capacity
11. Density
12. Standard state partial molar properties, if available

For any particular systems, the MSE parameters can be determined with as much as the available experimental data listed above to ensure the thermodynamic consistency of various properties. The inclusion of caloric data (i.e. heats of dilution and mixing, and heat capacity) can ensure the correct extrapolation of Gibbs energy, and hence, VLE and solubility, with temperature.

Simultaneous inclusion of various types of experimental data in regression has been made possible in the new regression program, REGRESS. The following discussion pertains to the use of REGRESS.

#### IV. CHEMISTRY MODEL SET UP

The chemistry model will be generated the same way it is generated using the conventional OLI framework, i.e. using OLI/Express or OLI/ESP. To invoke the MSE/H3O+ model, select “Mix Solvent (H3OION based)” from the “Select Thermodynamic Framework” page, which is now a default selection.

Similar to the regression in the conventional OLI framework, an EQUATIONS section is necessary if variables must be defined using the internal OLI variables. Some commonly used variable definitions in the MSE regression are given below.

Property	Definition
Water activity ( $a_{water}$ ):	DEFINE AWATER=EXP(AH2O+LH2O)
Mean activity coefficient ( $\gamma_{\pm}$ ) of a completely dissociated 1:1 electrolyte (e.g. KF)	DEFINE GAMMA=EXP(LH2O+(AKION+AFION)/2.0)

Explanations of these definitions and their differences from those in the conventional OLI framework are given in the next section.

## V. DEFINITION OF VARIABLES:

The following table lists some variables that are notably different in the MSE framework and in the conventional OLI framework. The differences in the two frameworks are compared.

MSE framework	Conventional OLI framework
<p>1. <i>Concentrations</i></p> <p>All of the concentrations are in mole-fraction. For example, in the H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O system, the variables, HION, SO4ION, HSO4ION, H2SO4AQ, SO3AQ, and H2O represent the <i>mole-fractions</i> for H<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>SO<sub>4</sub>(aq), SO<sub>3</sub>(aq), and H<sub>2</sub>O, respectively.</p>	<p>Concentrations are expressed by water-based molalities (mol/kg H<sub>2</sub>O). Variables, HION, SO4ION, HSO4ION, H2SO4AQ, and SO3AQ represent <i>molalities</i> of these species; while the water concentrations for all of the systems are always 55.509mol/1000 kg H<sub>2</sub>O.</p>
<p>2. <i>Water activity</i></p> <p>The natural logarithm of the water <i>activity coefficient</i> ( <math>\ln \gamma_{water}</math> ) is expressed by the variable AH2O. In order to determine the water <i>activity</i>, one needs to add in the chemistry model file:</p> <p>DEFINE AWATER=EXP(AH2O+LH2O)</p> <p>Where LH2O is the natural logarithm of the mole-fraction of H<sub>2</sub>O ( <math>\ln x_{water}</math> ).</p>	<p>The natural logarithm of the water <i>activity</i> ( <math>\ln a_{water}</math> ) is denoted by the variable AH2O. Therefore, in order to determine the water <i>activity</i>, one needs to add in the chemistry model file:</p> <p>DEFINE AWATER=EXP(AH2O)</p>
<p>3. <i>Activity Coefficients</i></p> <p>The variable AKION denotes the natural logarithms of the activity coefficient of K<sup>+</sup>, <math>\ln \gamma_{K^+}^{\infty,x}</math>, where <math>\gamma_{K^+}^{\infty,x}</math> is the mole-fraction based activity coefficient of K<sup>+</sup> in unsymmetrical normalization (i.e. infinite dilution in water as reference state). The relationship between <math>\gamma_{K^+}^{\infty,x}</math> and the conventional molality-based activity coefficient, <math>\gamma_i^{\infty,m}</math> is</p> $\gamma_j^{m,\infty} = x_w \cdot \gamma_j^{x,\infty}$ <p>Therefore, the mean activity coefficient of a completely dissociated electrolyte as determined by conventional definition can be defined in the chemistry model, for a 1:1 electrolyte such as KCl, as:</p> <p>DEFINE GAMMA=EXP(LH2O+(AKION+ACLION)/2.0)</p>	<p>The variable AKION represents the natural logarithm of the conventional molality-based activity coefficient for K<sup>+</sup>, <math>\ln(\gamma_{K^+}^{\infty,m})</math>. Therefore, the mean activity coefficient of a completely dissociated electrolyte as determined by conventional definition can be defined in the chemistry model, for a 1:1 electrolyte such as KCl, as:</p> <p>DEFINE GAMM=EXP((AKION+ACLION)/2.0)</p>
<p>4. <i>Equilibrium Constant</i></p> <p>For chemical reaction: MXAQ=MION+XION, the equilibrium constant, KMXAQ, is defined as that of mole-fraction based, infinite dilution in water reference state, i.e.</p> $K^{\infty,x} = \frac{x_M x_X}{x_{MX}} \cdot \frac{\gamma_M^{\infty,x} \gamma_X^{\infty,x}}{\gamma_{MX}^{\infty,x}}$ <p>relationship between <math>K^{\infty,x}</math> and <math>K^{\infty,m}</math> is</p> $\log K^{\infty,m} = \log K^{\infty,x} + \Delta n \cdot \log 55.509$ <p>where <math>\Delta n</math> is the change in number of moles in reaction (<math>\Delta n=1</math> in MXAQ=MION+XION). It should be noted that values for log Kfit in the databank are based on <math>\log K^{\infty,m}</math>.</p>	<p>The equilibrium constant, KMXAQ, is defined as that of molal-based, infinite dilution in water reference state, i.e.</p> $K^{\infty,m} = \frac{m_M m_X}{m_{MX}} \cdot \frac{\gamma_M^{\infty,m} \gamma_X^{\infty,m}}{\gamma_{MX}^{\infty,m}}$
<p>5. <i>Gibbs Energy of Transfer</i></p> <p>The Gibbs energy of transfer of LiCl from water to methanol can be derived as<sup>3</sup></p>	<p>Not available</p>

<sup>3</sup> Wang, P.; Anderko, A.; Young, R. D., Fluid Phase Equilibria, 203 (2002) 141-176.

$$\Delta_{tr}G_{LiCl}^0(w \rightarrow M) = 2RT \ln \left( \frac{\rho_w}{\rho_M} \right) + RT \left[ \ln \gamma_{Li^+, M}^{\infty, x} + \ln \gamma_{Cl^-, M}^{\infty, x} \right] + 2RT \ln \left( \frac{M_M}{M_w} \right)$$

where  $\gamma_{i, M}^{\infty, x}$  is the value of  $\gamma_i^{\infty, x}$  for ion i in pure methanol; and  $\rho_w$  and  $\rho_M$  are densities of pure water and pure methanol, respectively; and  $M_M$  and  $M_w$  are molar masses of methanol and water, respectively. Thus, the following definitions are necessary to calculate  $\Delta_{tr}G_{LiCl}^0(w \rightarrow M)$  at 298.15K:

```
DEFINE GTR1=8.3147*T*(ANAION+ACLION+2.0*LOG(32.0424/18.0152))
DEFINE GTR2=2.0*8.3147*T*(LOG(0.997/0.7866))
DEFINE GTRE=GTR1+GTR2
```

## VI. DATA STATEMENT SET UP FOR HEATS OF DILUTION AND MIXING

The inclusion of heats of mixing and dilution data in regression is the distinctive feature of the OLI/MSE. A majority of solution caloric data, especially those of aqueous electrolyte solutions, have been measured as heat of dilution. The data statement for heat of dilution is fixed such that for the dilution of aqueous HCl solutions, it is:

```
DATA T PT HCLIN H2OIN HCLIN H2OIN : HDILUT
      |initial_x| |final_x|
```

The first inflow (HCLIN and H2OIN) inputs the initial mole fractions of HCl and H2O, respectively, in HCl(aq) solution, and the second inflow gives the final mole fractions of these components; HDILUT is the heat of dilution in unit of cal/mol. It should be noted that the order of the components in the inflows (e.g. H2O and HCl) may be altered, but it must remain the same for the initial and final solutions.

The data statement for the heat of mixing also has a fixed format. Thus, the following statement is used for the mixing of two solutions that each contains methanol, H2O, and NaCl to form a mixture with final concentrations that are given in the 3<sup>rd</sup> inflow (the final mixture):

```
DATA T PT METHANOLIN H2OIN NACLIN METHANOLIN H2OIN NACLIN METHANOLIN H2OIN NACLIN : DHMIX
      |solution_1| |solution_2| |final_mixture|
```

In the 1<sup>st</sup> and the 2<sup>nd</sup> sets of inflows (METHANOLIN H2OIN NACLIN), the mole fractions of the three components are given for the two solutions that are mixed; the 3<sup>rd</sup> set of inflow gives the concentrations (mole fractions) of these components in the final mixture. DHMIX is the heat of mixing in unit of cal/mol. It should be noted that (1) the minimum number of components in each inflow (solution) is 2, and the maximum is 4 for the current OLI/MSE; (2) the order of the components (e.g. methanol, H2O, NaCl) may be altered, but it must remain the same in each of the three sets (i.e. solution 1, solution 2, final mixture); (3) in the cases that the mixing solution (solution 1 or solution 2) contains less components



than in the final mixture, simply input zero concentration for the component that is not present in the “solution”.

## V. DATA STATEMENT SET UP FOR Liquid-Liquid Equilibrium Data

The following DATA statement allows constraint on the LLE condition, i.e. equal activities of phenol (C6H5OHAQ) in aqueous phase and in phenol-rich liquid phase; and equal activities of H2O in aqueous and in phenol-rich phase at the given T and P:

```
DATA T PT C6H5OHIN H2OIN C6H5OHIN H2OIN : LLE_C6H5OHAQ LLE_H2O
```

In this statement, equilibrium concentrations of C6H5OH and H2O in the two liquid phases are given in the 1<sup>st</sup> {C6H5OHIN H2OIN} (e.g. in aqueous phase) and the 2<sup>nd</sup> {C6H5OHIN H2OIN} (e.g. in phenol-rich phase), respectively. Values of LLE\_C6H5OHAQ and LLE\_H2O are the ratio of the activities of phenol in the two liquid phases, and that of H2O in the two liquid phases, and therefore, must be set to 1.0.

Further constraints on the equilibrium concentrations at LLE can be achieved using the following DATA statement:

```
DATA T PT H2OIN C6H5OHIN :C6H5OHAQ H2O XC6H5OHAQO XH2OO
```

Where the variables after “:” give the equilibrium concentrations of phenol and H2O in aqueous phase, and phenol and H2O in organic phase. The {C6H5OHIN H2OIN} before “:” gives an initial composition of the phenol-water mixture that will be separated to form the two liquid phases.

## VI. EXAMPLES OF REGRESSION

The examples given below serve only as demonstrations of data regression using the OLI/MSE. In most cases, only a small portion of the data set used in the actual regressions is shown. The electronic files that contain chemistry model (MOD files) and input data (INR files) for each of the following examples are also provided for users to practice on OLI/MSE regression. The inflow concentrations are expressed as mole fraction in all of the examples; they can also be expressed as the number of moles in the inflow. For example, for aqueous systems, if the number of moles for water is given as 55.509, then the inflow concentrations for other species are the molalities (mol/kg H<sub>2</sub>O).

## Example 1. Methanol-water: VLE, heat of mixing, and heat capacity

### Model Set Up

The chemistry model is generated using OLI/Express or OLI/ESP. The inflow species are

H2O

METHANOL

The data to be regressed are PT (total vapor pressure), YMETHANOL (vapor phase mole-fraction of methanol), DHMIX (heat of mixing), and CP (heat capacity). There are no need to define variables in the model (.mod) file.

### Input File Set Up

The header section of the input file (MW.INR) contains the same information as that used in data regression with conventional OLI model, except that the parameters to be adjusted are those specific for the MSE model. In this case, the UNIQUAC interaction parameters for H2O-METHANOL are adjusted, together with the equilibrium constant for METHANOLVAP=METHANOLAQ. The input file looks like this:

```
$TITLE
Methanol-water VLE, heat of mixing, heat capacity
$CONTROL
MAXIT 100
QFIT 1.0E-6
METH 2
MARQ 1
SCALE 2.0
$PARAMETERS
P01 1.0 -3149.647 -10 10. H2O METHANOLAQ Q0IJ
P02 1.0 -2799.164 -10 10. H2O METHANOLAQ Q0JI
P03 1.0 24.43680 -10 10. H2O METHANOLAQ Q1IJ
P04 1.0 8.180557 -10 10. H2O METHANOLAQ Q1JI
P05 1.0 -1.0469214E-02 -10 10. H2O METHANOLAQ Q2IJ
P06 1.0 -1.9480291E-02 -10 10. H2O METHANOLAQ Q2JI
P07 1.0 -8.197316 -10. 10. KMETHANOLVAP A
P08 1.0 2790.851 -10. 10. KMETHANOLVAP B
P09 1.0 2.2662951E-03 -10. 10. KMETHANOLVAP C
P10 1.0 4.8065231E-06 -10. 10. KMETHANOLVAP D
$DATA SET 1
FREE PT
FIX V 1.0E-08
DATA T METHANOLIN H2OIN : PT YMETHANOL
25 0.0202 0.9798 0.0351 0.1441
25 0.0403 0.9597 0.0395 0.2557
25 0.062 0.938 0.0447 0.3463
25 0.0791 0.9209 0.0478 0.416
25 0.1145 0.8855 0.0561 0.5047
25 0.2017 0.7983 0.0727 0.6474
25 0.3973 0.6027 0.0992 0.7904
25 0.6579 0.3421 0.1266 0.8908
25 0.8137 0.1863 0.1446 0.9521
25 1 0 0.1666 1
100 0.0022 0.9978 1.0275 0.0192
100 0.035 0.965 1.2249 0.191
100 0.074 0.926 1.4085 0.313
100 0.163 0.837 1.7419 0.496
```

100	0.352	0.648	2.1366	0.662
100	0.522	0.478	2.4769	0.75
100	0.667	0.333	2.7830	0.824
100	0.826	0.174	3.0756	0.911
100	0.946	0.054	3.3274	0.976
100	0.958	0.042	3.3274	0.981
0	1	0	0.0405	1
25	1	0	0.1658	1
50	1	0	0.5492	1
65	1	0	1.0197	1
95.33	1	0	3.0000	1
128.66	1	0	8.0002	1
170	1	0	20.712	1
200	1	0	37.843	1

\$DATA SET 2

FREE PT

FIX V 1.0E-08

DATA	T	PT	METHANOLIN	H2OIN	METHANOLIN	H2OIN	METHANOLIN	H2OIN	:	DHMIX
50	1	1	1	0	0	1	0.0237	0.9763		-26.506
50	1	1	1	0	0	1	0.0939	0.9061		-91.707
50	1	1	1	0	0	1	0.1817	0.8183		-133.198
50	1	1	1	0	0	1	0.2903	0.7097		-152.390
50	1	1	1	0	0	1	0.3886	0.6114		-157.003
50	1	1	1	0	0	1	0.5229	0.4771		-146.989
50	1	1	1	0	0	1	0.7654	0.2346		-98.112
50	1	1	1	0	0	1	0.8735	0.1265		-63.695
50	1	1	1	0	0	1	0.9541	0.0459		-26.004
25	1	1	1	0	0	1	0.00107	0.99893		-1.785
25	1	1	1	0	0	1	0.00412	0.99588		-6.845
25	1	1	1	0	0	1	0.016	0.984		-26.341
25	1	1	1	0	0	1	0.0641	0.9359		-96.489
25	1	1	1	0	0	1	0.1358	0.8642		-166.907
25	1	1	1	0	0	1	0.3172	0.6828		-211.759
25	1	1	1	0	0	1	0.571	0.429		-178.881
25	1	1	1	0	0	1	0.7516	0.2484		-132.643
25	1	1	1	0	0	1	0.8637	0.1363		-84.116
25	1	1	1	0	0	1	0.9622	0.0378		-26.859
25	1	1	1	0	0	1	0.9805	0.0195		-14.345
25	1	1	1	0	0	1	0.99	0.01		-7.550
25	1	1	1	0	0	1	0.996	0.004		-3.411

\$DATA SET 3

FREE PT

FIX V 1.0E-08

DATA	T	PT	H2OIN	METHANOLIN	:	CP
25	1	1	0.0	1.0		0.6053
25	1	1	0.04183	0.95817		0.61619
25	1	1	0.15329	0.84671		0.65253
25	1	1	0.25247	0.74753		0.68719
25	1	1	0.35174	0.64826		0.72579
25	1	1	0.49462	0.50538		0.78764
25	1	1	0.59988	0.40012		0.84010
25	1	1	0.70108	0.29892		0.89673
25	1	1	0.85506	0.14494		0.98270
25	1	1	0.97097	0.02903		1.00583
25	1	1	0.99061	0.00939		1.00175

END

**Example 2. NaCl-water: water activity, osmotic coefficient, solubility, heat of dilution, heat capacity, density**

This example determines the interaction parameters between  $\text{Cl}^-$  and  $\text{Na}^+$  using simultaneously water activity, osmotic coefficient, solubility, heat of dilution, heat capacity, and density data for NaCl-water system. The inflow species are

H2O

NACL

Vapor phase and all solids (NACL PPT and NACL.2H2O) are included in the chemistry model. Because the osmotic coefficient is not an internal OLI variable, its definition must be included in the chemistry model:

$$\phi = -\frac{m_w}{\sum_i \nu_i m_i} \ln a_w = -\frac{x_w}{2x_{\text{NaCl}}} \ln a_w$$

The following section is added to the model file:

EQUATIONS

DEFINE PHI=-(AH2O+LH2O)\*H2OIN/(2.0\*NACLIN)

DEFINE AW=EXP(AH2O+LH2O)

The 1<sup>st</sup> DEFINE calculates osmotic coefficient of NaCl in the aqueous solution, the 2<sup>nd</sup> defines water activity. The parameters to be adjusted are those of the middle-range interactions between  $\text{Cl}^-$  and  $\text{Na}^+$ , together with the standard state entropies and Gibbs free energies of formation of NaCl(aq), NaCl(s), and NaCl.2H<sub>2</sub>O. Three ELEM statements are added to automatically calculate standard state enthalpies of formation for these species based on the adjusted GREF (or GRFS) and SREF (or SRFS). The solubility is determined at scaling index of a particular solid phase (SC\_SOLID) to be unity. Therefore, a SC\_SOLID value of 1.0 is the objective at the experimental saturated solutions of NaCl. The statement SC\_INDEX H2OPPT NACL PPT NACL.2H2O indicates that only scaling index is calculated for the listed solids. The input file (NACL.INR) is as follows.

```
$TITLE
NaCl
$CONTROL
MAXIT 0
METH 1
$PARAMETERS
P01 1.0 -324.215      -10 10 CLION NAION BMD0
P02 1.0  0.945176    -10 10 CLION NAION BMD1
P03 1.0  29640.8     -10 10 CLION NAION BMD2
P04 1.0 -8.95755E-04 -10 10 CLION NAION BMD3
P05 1.0  369.847     -10 10 CLION NAION CMD0
P06 1.0 -1.18527     -10 10 CLION NAION CMD1
P07 1.0 -28505.9     -10 10 CLION NAION CMD2
P08 1.0  1.22898E-03 -10 10 CLION NAION CMD3
P09 1.0 -84120.6     -10 10 NACL AQ  GREF
P10 1.0  50.5222     -10 10 NACL AQ  SREF
```

P11 1.0 -91842.0 -10 10 NACL PPT GRFS  
 P12 1.0 17.1419 -10 10 NACL PPT SRFS  
 P13 1.0 -205339.6 -10 10 NACL.2H2O GRFS  
 P14 1.0 43.5014 -10 10 NACL.2H2O SRFS  
 P15 1.0 2.799165 -10 10 NAION CLION DMD1  
 P16 1.0 -3.954531 -10 10 NAION CLION DMD2  
 P17 1.0 2.1220225E-02 -10 10 NAION CLION DMD3  
 P18 1.0 -1.5020390E-02 -10 10 NAION CLION DMD4  
 P19 1.0 1.9914062E-05 -10 10 NAION CLION DMD5  
 P20 1.0 -2.8257865E-05 -10 10 NAION CLION DMD6  
 P21 1.0 -0.3509673 -10 10 H2O NACLAQ DMD1  
 P22 1.0 0.2678358 -10 10 H2O NACLAQ DMD2  
 ELEM NACLAQ 1.0 12.26 0.5 53.29  
 ELEM NACL PPT 1.0 12.26 0.5 53.29  
 ELEM NACL.2H2O 1.0 12.26 0.5 53.29 2.0 31.21 1.0 49.0

\$DATA SET 1

FREE PT

FIX V 1.0E-10

DATA	T	PT	NACLIN	H2OIN	NACLIN	H2OIN	:	HDILUT
100		1	0.097547	0.902453	0.048346	0.951654		-400.813
100		1	0.082632	0.917368	0.041047	0.958953		-324.331
100		1	0.067217	0.932783	0.033449	0.966551		-259.560
100		1	0.048346	0.951654	0.024121	0.975879		-198.136
100		1	0.024121	0.975879	0.012051	0.987949		-144.120
100		1	0.016708	0.983292	0.008353	0.991647		-128.824
100		1	0.012051	0.987949	0.006026	0.993974		-118.786
100		1	0.010238	0.989762	0.005119	0.994881		-114.245
100		1	0.006026	0.993974	0.003012	0.996988		-100.860

\$DATA SET 2

SC\_INDEX H2OPPT NACL PPT NACL.2H2O

DATA	T	PT	H2OIN	NACLIN	:	PHI	AW
25.00	1.03		0.9999820	0.0000180		0.9884	1.0000
25.00	1.03		0.9999640	0.0000360		0.9840	0.9999
25.00	1.03		0.9991000	0.0009000		0.9434	0.9983
25.00	1.03		0.9857925	0.0142075		0.9298	0.9736
25.00	1.03		0.9618773	0.0381227		0.9985	0.9239
25.00	1.03		0.9552560	0.0447440		1.0229	0.9086
25.00	1.03		0.9265545	0.0734455		1.1469	0.8337
25.00	1.03		0.9113423	0.0886577		1.2225	0.7883
25.00	1.03		0.9024523	0.0975477		1.2695	0.7600

\$DATA SET 3

SC\_INDEX H2OPPT NACL PPT NACL.2H2O

WEIGHT 0.5

DATA	T	PT	H2OIN	NACLIN	:	CP
200.00	17.87		0.9823035	0.0176965		0.9864
200.00	17.87		0.9652225	0.0347775		0.9238
200.00	17.87		0.9487253	0.0512747		0.8748
200.00	17.87		0.9327826	0.0672174		0.8354
200.00	17.87		0.9173668	0.0826332		0.8031
200.00	17.87		0.9024523	0.0975477		0.7758
200.00	17.87		0.8809683	0.1190317		0.7412

\$DATA SET 4

SC\_INDEX H2OPPT NACL PPT NACL.2H2O

DATA	T	PT	H2OIN	NACLIN	:	SC_NACL.2H2O
-21.20	1.00		0.9143762	0.0856238		1.0
-15.00	1.00		0.9099589	0.0900411		1.0
-10.00	1.00		0.9068227	0.0931773		1.0
-5.00	1.00		0.9038776	0.0961224		1.0
0.00	1.01		0.9009000	0.0991000		1.0

\$DATA SET 5

SC\_INDEX H2OPPT NACL PPT NA CL.2H2O  
DATA T PT H2OIN NA CLIN : SC\_NACL PPT  
0.00 1.01 0.9009921 0.0990079 1.0  
20.00 1.03 0.9005313 0.0994687 1.0  
50.00 1.13 0.8984478 0.1015522 1.0  
100.00 2.10 0.8920056 0.1079944 1.0  
150.00 6.16 0.8847759 0.1152241 1.0  
200.00 17.87 0.8753427 0.1246573 1.0  
250.00 44.13 0.8624360 0.1375640 1.0

\$DATA SET 6

FREE PT  
FIX V 1.0E-10  
DATA T PT NA CLIN H2OIN : DENMAS  
0 1 0.000180 0.999820 1000.3  
0 1 0.008927 0.991073 1021.6  
0 1 0.017696 0.982304 1042.2  
0 1 0.034777 0.965223 1080.5  
0 1 0.051274 0.948726 1115.8  
0 1 0.067217 0.932783 1148.3  
0 1 0.082632 0.917368 1178.6  
0 1 0.097547 0.902453 1207  
100 1 0.000180 0.999820 958.8  
100 1 0.008927 0.991073 977.6  
100 1 0.017696 0.982304 996.1  
100 1 0.034777 0.965223 1030.9  
100 1 0.051274 0.948726 1063.4  
100 1 0.067217 0.932783 1093.7  
100 1 0.082632 0.917368 1122.2  
100 1 0.097547 0.902453 1149

END

### Example 3. NaCl-methanol-water: VLE, solubility, Gibbs energy of transfer, heat of mixing

This example will determine the middle-range interaction parameters using the experimental VLE, solubility, Gibbs energy of transfer, and heat of mixing data of NaCl-water-methanol mixtures. The inflow contains three components:

H2O  
NACL  
METHANOL

Prior to running regression for this case, the interaction parameters for methanol/water, Na<sup>+</sup>/Cl<sup>-</sup> have been obtained from the fitting of experimental data for the binary systems (e.g. methanol-water and NaCl-water), and the standard state properties that affect solubilities of NaCl have also been determined, as shown in Examples 1 and 2, and these parameters has been placed in the **MIXSOL** databank before the chemistry model is generated. The following section is added to the model file to define the standard Gibbs energy of transfer of Na<sup>+</sup> and Cl<sup>-</sup> from water to methanol ( $\Delta_{tr}G^0_{Na^+}=8$  kJ/mol,  $\Delta_{tr}G^0_{Cl^-}=13$  kJ/mol):

EQUATIONS

DEFINE GTRNA=8.3147\*T\*(ANAION+LOG(32.0424/18.0152)+LOG(0.997/0.7866))

DEFINE GTRCL=8.3147\*T\*(ACLION+LOG(32.0424/18.0152)+LOG(0.997/0.7866))

In these definitions, 32.0424 is the molar weight of methanol, 0.997 and 0.7866 are densities of water and methanol, respectively, at 298.15K (cf. **V. DEFINITION OF VARIABLES**). The INR file (MWNACL.INR) is given as follows.

\$TITLE

NaCl-Methanol-water VLE, Gibbs energy of transfer, solubility, heat of mixing

\$CONTROL

MAXIT 100  
QFIT 1.0E-6  
METH 2  
MARQ .1  
SCALE 2.0

\$PARAMETERS

P01 1.0 -9.993176 -1 1. METHANOLAQ NAION BMD0  
P02 1.0 -6.1025114E-03 -1 1. METHANOLAQ NAION BMD1  
P03 1.0 -910.5254 -1 1. METHANOLAQ NAION BMD2  
P04 1.0 22.99711 -1 1. METHANOLAQ NAION CMD0  
P05 1.0 -6.8829476E-02 -1 1. METHANOLAQ NAION CMD1  
P06 1.0 3836.936 -1 1. METHANOLAQ NAION CMD2  
P07 1.0 -53.37051 -1 1. CLION METHANOLAQ BMD0  
P08 1.0 0.1522164 -1 1. CLION METHANOLAQ BMD1  
P09 1.0 2953.091 -1 1. CLION METHANOLAQ BMD2  
P10 1.0 64.24360 -1 1. CLION METHANOLAQ CMD0  
P11 1.0 -0.1310526 -1 1. CLION METHANOLAQ CMD1  
P12 1.0 -8792.215 -1 1. CLION METHANOLAQ CMD2

\$DATA SET 1

FREE PT

FIX V 1.0E-08

DATA T	METHANOLIN	NACLIN	H2OIN	:	PT	YMETHANOL
99.60	0.026	0.099	0.875		1.0026	0.259
95.00	0.045	0.095	0.860		1.0026	0.418
90.50	0.067	0.089	0.844		1.0026	0.518
86.50	0.101	0.083	0.816		1.0026	0.590
82.30	0.161	0.073	0.766		1.0026	0.661
79.00	0.235	0.060	0.705		1.0026	0.721

76.20	0.332	0.046	0.622	1.0026	0.766
74.00	0.433	0.033	0.534	1.0026	0.804
72.20	0.544	0.023	0.433	1.0026	0.841
70.20	0.643	0.016	0.341	1.0026	0.875
68.00	0.760	0.010	0.230	1.0026	0.913
66.10	0.874	0.005	0.121	1.0026	0.953
64.20	0.998	0.002	0.000	1.0026	1.000

\$DATA SET 2

WEIGHT	100.0				
DATA T PT	METHANOLIN	H2OIN	NACLIN	:	GTRNA
25. 1.0	0.99999999	0.0	1.0E-8		8000.

\$DATA SET 3

WEIGHT	100.0				
DATA T PT	METHANOLIN	H2OIN	NACLIN	:	GTRCL
25. 1.0	0.99999999	0.0	1.0E-8		13000.

\$DATA SET 4

FREE	NACLIN				
FIX	NACLPPT	1.0E-6			
DATA T PT	METHANOLIN	H2OIN	:	NACLIN	
50 1	0.9931909	0		0.0068091	
50 1	0.825997	0.1632201		0.0107829	
50 1	0.6802285	0.3026013		0.0171702	
50 1	0.4416286	0.5236194		0.034752	
50 1	0.3435662	0.6110532		0.0453806	
50 1	0.2573137	0.686385		0.0563012	
50 1	0.1135393	0.8076265		0.0788343	
50 1	0.053499	0.8563005		0.0902004	
50 1	0	0.8982856		0.1017144	

\$DATA SET 5

DATA T PT	METHANOLIN	H2OIN	NACLIN	METHANOLIN	H2OIN	NACLIN	METHANOLIN	H2OIN	NACLIN	:	DHMIX
12.5 1	1	0	0	0	0.99689	0.00311	0.05	0.947051	0.002949		-87.930
12.5 1	1	0	0	0	0.99689	0.00311	0.1	0.897206	0.002794		-151.936
12.5 1	1	0	0	0	0.99689	0.00311	0.2	0.797517	0.002483		-215.225
12.5 1	1	0	0	0	0.99689	0.00311	0.3	0.697827	0.002173		-229.087
12.5 1	1	0	0	0	0.99689	0.00311	0.4	0.598138	0.001862		-221.343
12.5 1	1	0	0	0	0.99689	0.00311	0.5	0.498448	0.001552		-205.043
12.5 1	1	0	0	0	0.99689	0.00311	0.6	0.398758	0.001242		-182.935
12.5 1	1	0	0	0	0.99689	0.00311	0.7	0.299069	0.000931		-154.159
12.5 1	1	0	0	0	0.99689	0.00311	0.8	0.199379	0.000621		-116.778
12.5 1	1	0	0	0	0.99689	0.00311	0.9	0.099690	0.000310		-66.898

END



#### Example 4. Acetic Acid-Ethanol: VLE data

This example will fit the UNIQUAC parameters for acetic acid/ethanol to the VLE data of acetic acid-ethanol system. The inflow has three components:

H2O

ACETACID

ETHANOL

It should be noted that H2O is always in the inflow when the chemistry model is generated although it may not be a component in the system of interest. In this case, the concentration of H2O can always be set to be zero. Although the MSE model is on mole-fraction basis and has a symmetrical reference state, the activity coefficients in the MSE framework are converted to those based on the conventional reference state, i.e. infinite dilution in water, for the appropriate speciation computation using the standard state properties in the existing OLI thermodynamic database. This conversion requires using appropriate interaction parameters between H<sub>2</sub>O and the species of interest. Before running regression in this case, the interaction parameters for ethanol/water and acetic acid/water must have been determined from the experimental data for these binary systems, and have been placed in the **MSEPUB** databank before the chemistry model is generated. The following is the input file EHAC.INR.

```
$TITLE
  acetic acid-ethanol system (VLE)
$CONTROL
  MAXIT 100
  METH 0
  MARQ 1.
  QFIT 1.0E-06
  SCALE 2
  OBJEC 1
$PARAMETERS
P01  1.0 7261.531          -10 10. ACETACIDAQ ETHANOLAQ Q0IJ
P02  1.0 -21.33661        -10 10. ACETACIDAQ ETHANOLAQ Q1IJ
P03  1.0 -1.2471179E-02  -10 10. ACETACIDAQ ETHANOLAQ Q2IJ
P04  1.0 9739.199         -10 10. ACETACIDAQ ETHANOLAQ Q0JI
P05  1.0 -91.17781        -10 10. ACETACIDAQ ETHANOLAQ Q1JI
P06  1.0 0.1901734        -10 10. ACETACIDAQ ETHANOLAQ Q2JI
$DATA SET 1
  FREE PT
  FIX V      1.0E-10
DATA  T      ACETACIDIN  ETHANOLIN  : YETHANOL  PT
      45      1          0          0          0.0574
      45      0.94      0.06      0.116      0.0628
      45      0.914     0.086     0.163     0.0651
      45      0.869     0.131     0.241     0.0696
      45      0.801     0.199     0.366     0.0778
      45      0.704     0.296     0.525     0.0898
      45      0.593     0.407     0.69      0.1045
      45      0.497     0.503     0.809     0.1217
      45      0.406     0.594     0.888     0.1409
      45      0.306     0.694     0.938     0.161
      45      0.238     0.762     0.962     0.1742
      115.05   0.915     0.085     0.161     1
      112.3    0.846     0.154     0.28      1
```

109.4	0.762	0.238	0.416	1
106.8	0.71	0.29	0.503	1
102.8	0.623	0.377	0.631	1
101	0.553	0.447	0.692	1
95	0.443	0.557	0.816	1
93.9	0.393	0.607	0.847	1
88.5	0.275	0.725	0.925	1
83.4	0.154	0.846	0.972	1
80.2	0.069	0.931	0.991	1

END

### Example 5. Dissociation of Acidic Acid in Ethanol-Water Mixtures

This example determines the interaction between acetate ion (ACETATEION) and ethanol using the experimental dissociation constants of acetic acid in ethanol-water mixtures. Before running regression in this case, the interaction parameters for ethanol/water, ethanol/acetic acid, and acetic acid/water have been determined from the experimental data for the three binary systems, and have been placed in the **MSEPUB** databank before the chemistry model in this case is generated.

Since the experimental data are the mixed-solvent based “apparent ionization constants”, they must be expressed using the species equilibrium concentrations. The expression is derived following the definition of the “apparent ionization constant” on the mixed-solvent basis:

$$K_A^{app} = \frac{1000 \cdot x_{H^+} x_{A^-}}{x_{HA} (M_w x_w + M_E x_E)}$$

where the subscripts,  $H^+$ ,  $A^-$ ,  $HA$ ,  $w$ , and  $E$ , denote proton, acetate ion, associated acetic acid neutral species, water, and ethanol, respectively;  $M_w$  and  $M_E$  are molar weight of water (18.0152) and ethanol (46.0694);  $x_k$  is the mole fraction of species  $k$  at equilibrium. The  $K_A^{app}$  must be defined in the model set up. The following section is added in the chemistry model file:

EQUATIONS

DEFINE AK1=LHION+LACETATEION-LACETACIDAQ

DEFINE AK2=6.90776-LOG(18.0152\*H2O+46.0694\*ETHANOLAQ)

DEFINE AK=AK1+AK2

The first DEFINE evaluates  $AK1 = \ln x_{H^+} + \ln x_{A^-} - \ln x_{HA}$ ; the second DEFINE evaluates

$AK2 = \ln(1000) - \ln(M_w x_w + M_E x_E)$ ; the natural logarithm of the apparent ionization constant,  $\ln K_A^{app}$ , is defined by  $AK$ , and is the target of the regression. The acetic acid concentrations are assumed to be  $1 \times 10^{-4}$  mol/kg solvent at all solvent compositions, and then converted to mole fractions in the following case file (EHACW.INR). Both UNIQUAC and middle-range interaction parameters for ACETATEION/ETHANOLAQ are adjusted in this example.

\$TITLE

HAc-ETOH-WATER

\$CONTROL

MAXIT 1

METH 0

MARQ 50

QFIT 1.0E-06

SCALE 2

OBJEC 1

\$PARAMETERS

P01 1.0 17010.90 -10. 10. ACETATEION ETHANOLAQ Q0IJ

P02 1.0 10865.89 -10. 10. ACETATEION ETHANOLAQ Q0JI

P03 1.0 -0.1643104 -1. 1. ACETATEION ETHANOLAQ BMD0

\$DATA SET 1

DATA T PT ACETACIDIN H2OIN ETHANOLIN : AK

25	1	1.80E-06	1.0000	0.0000	-10.9603
25	1	1.80E-06	1.0000	0.0000	-10.9373
25	1	1.87E-06	0.9750	0.0250	-11.1675
25	1	1.89E-06	0.9669	0.0331	-11.0754
25	1	1.94E-06	0.9512	0.0488	-11.3978
25	1	2.00E-06	0.9294	0.0706	-11.2827
25	1	2.00E-06	0.9283	0.0717	-11.6050
25	1	2.06E-06	0.9094	0.0906	-11.8123
25	1	2.06E-06	0.9069	0.0931	-11.8353
25	1	2.18E-06	0.8663	0.1337	-12.2267
25	1	2.28E-06	0.8298	0.1702	-12.5951
25	1	2.29E-06	0.8267	0.1733	-12.5030
25	1	2.46E-06	0.7642	0.2358	-13.1478
25	1	2.59E-06	0.7181	0.2819	-13.4471
25	1	2.62E-06	0.7091	0.2909	-13.5622
25	1	2.75E-06	0.6604	0.3396	-13.9306
25	1	2.87E-06	0.6185	0.3815	-14.2760
25	1	2.98E-06	0.5814	0.4186	-14.5523
25	1	2.98E-06	0.5782	0.4218	-14.4833
25	1	3.07E-06	0.5484	0.4516	-14.8056
25	1	3.22E-06	0.4936	0.5064	-15.2431
25	1	3.51E-06	0.3915	0.6085	-15.8188
25	1	4.61E-06	0.0000	1.0000	-23.7627

END