

g^E Parameters from GC Methods

UNIQUAC, NRTL, Wilson, Margules,
original UNIFAC, modified UNIFAC (Dortmund), NIST-modified UNIFAC,
COSMO Models



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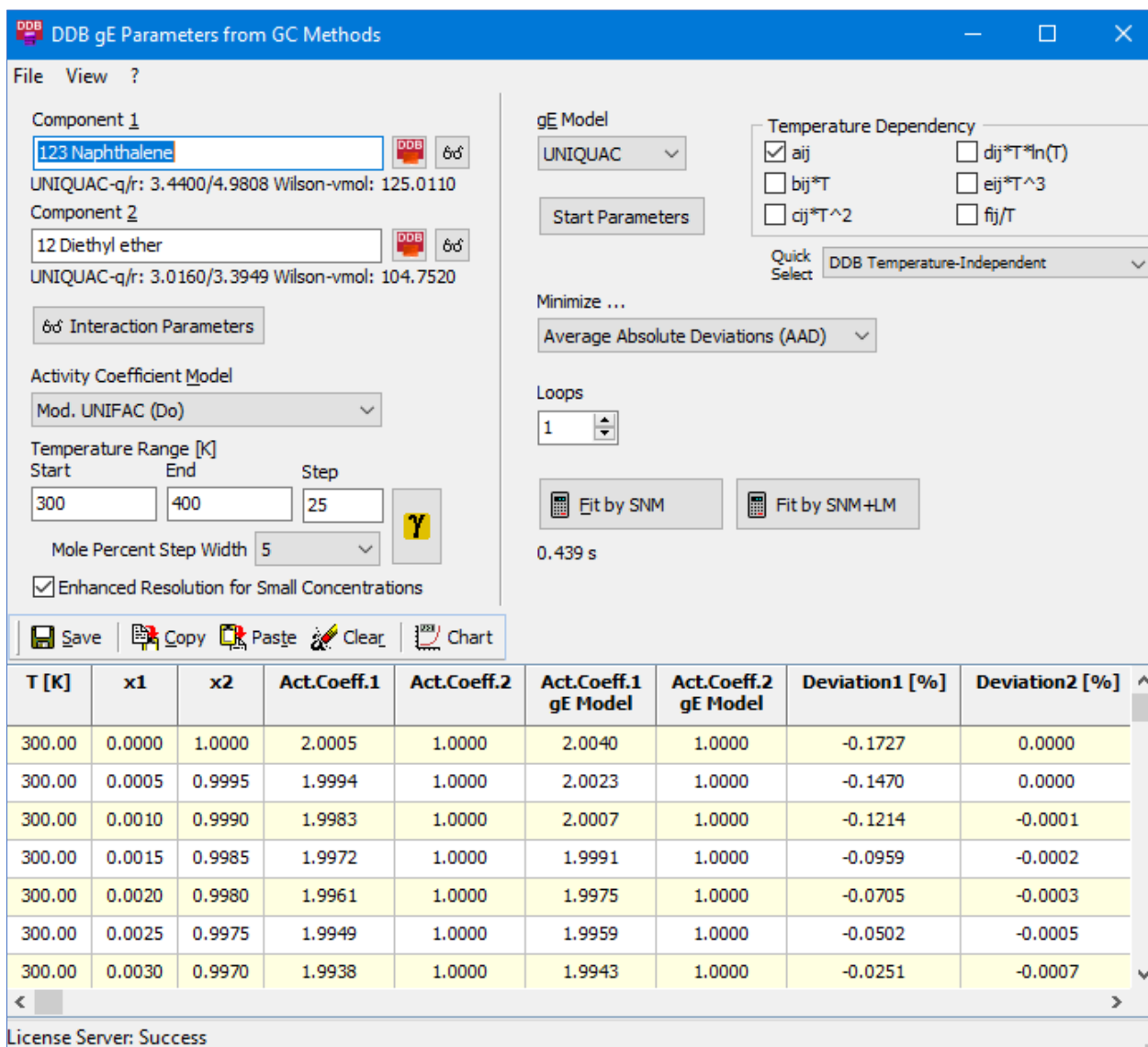
Contents

1	Introduction	3
2	Component Selection.....	4
3	Calculating Activity Coefficients	5
4	Fitting.....	6
4.1	Starting Values	6
4.2	Objective Function.....	6
4.3	Loops.....	6
4.4	Fitting.....	6
4.5	Batch Fitting.....	7
5	Results	9
5.1	Recalculated Values	9
5.2	Parameters.....	10
5.3	Save in the Parameter DDB	11
5.4	Save as Aspen INP Files	11
6	Appendix	12
6.1	Conversion between DDB and Aspen Simulator Equations	12
6.1.1	Introduction	12
6.1.2	Wilson	12
6.1.2.1	DDB Form	12
6.1.2.2	Aspen Form	12
6.1.2.3	Conversion between DDB and Aspen Parameters	12
6.1.3	NRTL.....	13
6.1.3.1	DDB Form	13
6.1.3.2	Aspen Form	13
6.1.3.3	Conversion between DDB and Aspen Forms	14
6.1.4	UNIQUAC	15
6.1.4.1	DDB Form	15
6.1.4.2	Aspen Form	15
6.1.4.3	Conversion between DDB and Aspen Form.....	16

1 Introduction

This program fits g^E model (Wilson, NRTL, Margules, and UNIQUAC) parameters to activity coefficients obtained from group contribution models (original UNIFAC, modified UNIFAC (Dortmund), modified UNIFAC (Lyngby), and NIST–modified UNIFAC) and some COSMO models for binary systems.

This software can obtain parameters for a high number of systems in a short time.



The screenshot shows the main dialog of the software. The components are 123 Naphthalene and 12 Diethyl ether. The gE Model is set to UNIQUAC. The temperature range is from 300 K to 400 K with a step of 25 K. The activity coefficient model is Mod. UNIFAC (Do). The fit is performed by SNM+LM, taking 0.439 s. The table below shows the results of the fit.

T [K]	x1	x2	Act.Coeff.1	Act.Coeff.2	Act.Coeff.1 gE Model	Act.Coeff.2 gE Model	Deviation1 [%]	Deviation2 [%]
300.00	0.0000	1.0000	2.0005	1.0000	2.0040	1.0000	-0.1727	0.0000
300.00	0.0005	0.9995	1.9994	1.0000	2.0023	1.0000	-0.1470	0.0000
300.00	0.0010	0.9990	1.9983	1.0000	2.0007	1.0000	-0.1214	-0.0001
300.00	0.0015	0.9985	1.9972	1.0000	1.9991	1.0000	-0.0959	-0.0002
300.00	0.0020	0.9980	1.9961	1.0000	1.9975	1.0000	-0.0705	-0.0003
300.00	0.0025	0.9975	1.9949	1.0000	1.9959	1.0000	-0.0502	-0.0005
300.00	0.0030	0.9970	1.9938	1.0000	1.9943	1.0000	-0.0251	-0.0007

Figure 1: Main dialog

The deviation does normally not exceed 1 percent (absolute mean error in the activity coefficients).

The software is integrated in the standard DDB software package using the DDB's component list, the parameter files, and the standard software components.

2 Component Selection

This part of the main dialog allows the specification of the binary system, either by DDB Components or by typing a known DDB component number.

Below each component, the program displays some data relevant data for some of the g^E models:

- UNIQUAC: Molecular surface and volume
- Wilson: Liquid volume at approx. 298 K

If any of these values are zero the corresponding model cannot be used.

The values are stored in the basic component file and can be modified by DDB Components.

The two buttons with glasses at the right side of the component names open a dialog with additional information about necessary component specific data.

The UNIQUAC volumes and surfaces and the Wilson volume are repeated here but the lines about the group assignment (group numbers and names) for the supported group contribution models add new important information. These groups must be available for all the components. Otherwise, a group contribution model cannot be used.

The „*Interaction Parameters*” button opens a dialog with information of the availability of group assignments and interaction parameters for the different group contribution methods.

Green lines indicate that this model can be used to calculate activity coefficients – group assignment and interaction parameters are available. Red lines indicate either a missing group assignment or missing interaction parameters. The “*Details*” page allows the user to identify the problem.

3 Calculating Activity Coefficients

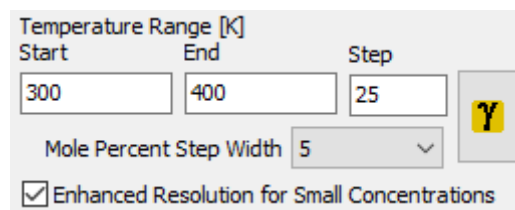
Several models are available for the calculation of activity coefficients:

- UNIFAC
- UNIFAC-MCM
- Mod. UNIFAC (Dortmund)
- NIST-modified UNIFAC
- modified UNIFAC (Lyngby)
- COSMO-RS (OI)
- COSMO-SAC
- COSMO-SAC 2010
- COSMO-SAC 2013

For the models UNIFAC and mod. UNIFAC (Dortmund) the UNIFAC consortium (www.unifac.org) maintains an extended list of groups and parameters, which are available for the consortium members only.

The program recalculates the activity coefficient table on any model change and displays an error message if a calculation fails because of missing parameters or group assignments.

The last settings are the temperature range and the step width of the composition.



Temperature Range [K]
Start End Step
300 400 25
Mole Percent Step Width 5
 Enhanced Resolution for Small Concentrations

Figure 2: Temperature Range

If the “*Enhanced Resolution for Small Concentrations*” option is set, the step width above 90 % and below 10 % is divided by a factor of 10 (e. g. from 5% to 0.5%) and the step width above 99% and below 1% is divided by a factor of 100 (e. g. from 5% to 0.05%).

If any of these values is changed, the γ button has to be used to force the program to recalculate the activity coefficient table.

4 Fitting

The program enables the fit of parameters for the g^E models UNIQUAC, NRTL, Wilson. Use the “ g^E Model” selector to switch the model.

For all three methods the temperature dependence of the parameters can be set to

$$a_j + b_j * T + c_j * T^2 + d_j * T * \ln(T) + e_j * T^3 + \frac{f_j}{T}$$

In the “Temperature Dependency” area, the parameters can be switched on and off.

The “Quick Select” combo box defines some short cuts to often used parameter sets.

4.1 Starting Values

Use the “Start Parameters” button to modify the starting values for the parameters in a new dialog.

The grid is editable and allows starting values to enter as well as initial step widths. A parameter can be fixed by setting the initial step to “0” or, better, by checking the “Constant” check box.

The “Latest Values” button allows using the parameters from the last fit and the “Standard Values” button resets the parameters to some useful preset values.

With the “ParameterDDB”- button it is possible to search the DDB parameter data bank for existing parameters and to select these parameters as starting values.

Fixing the NRTL α parameter can either be done by simply setting the step width to zero or by checking “Constant” - this works exactly the same as for the normal parameters. Setting a variable α is done by entering an initial step different to zero or by unchecking “Constant”.

The last possible setting is to limit α to a maximum and minimum value.

4.2 Objective Function

In the “Minimize” area the objective function can be set to

- Average Absolute Deviations
- Root Mean Square Deviations
- Mean Relative Deviation

All three objective functions have different advantages and downsides.

4.3 Loops

The “Loops” setting is used to restart the fit procedure up to four times. This is a useful and often necessary feature because the changes in the objective function are rather small near the minimum and the optimization process is starving before reaching a *global* minimum. The re-start uses the obtained parameters from the previous fit but starts with the step widths of the initial fit.

This procedure guarantees in many cases a better minimum (in deviations) than a single fit.

4.4 Fitting

The “Fit SNM” and “Fit by SNM+LM”- buttons start the fit. The used algorithm is Simplex-Nelder-Mead (SNM) or a combined Simplex-Nelder-Mead and Levenberg-Marquardt (LM). This SNM optimization algorithm is known to be robust and will not fail. The drawback of this stability is that the SNM method needs a lot of function calls and can be slow. LM is far quicker but tends to fail in

more cases.

The currently obtained objective function value and the parameters are displayed in a separate window.

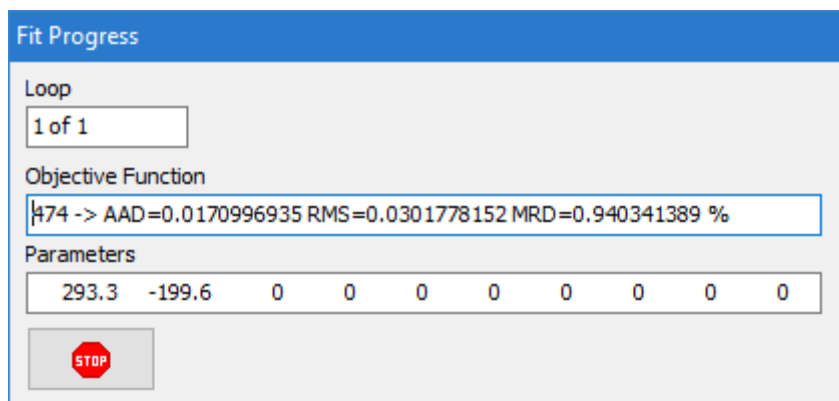


Figure 3: Fit Progress

The “STOP”- button allows stopping the current fit process.

The sequence of the parameters is always

- NRTL α first (if NRTL has been selected)
- A_{12} and A_{21} (temperature-independent parameter)
- B_{12} and B_{21} (linear temperature-dependent parameter)
- C_{12} and C_{21} (quadratic temperature-dependent parameter)
- and so on

4.5 Batch Fitting

The program can fit multiple systems in a row. These systems will be built from component lists, which can be created by other DDB software like the component management program, the Artist structure editor, or the DDB main retrieval program.

The dialogs

#	#DDB	Name
1	31	Benzene
2	59	Divinylbenzene
3	121	alpha-Methyl styrene
4	123	Naphthalene
5	150	Styrene
6	415	1-Phenylnaphthalene
7	471	Biphenyl
8	521	m-Terphenyl
9	763	tert-Butylbenzene
10	797	2-Phenyl-2,4,6-trimethylheptane
11	925	Anthracene

Figure 4: List of Components

#	Component1	Component2	Fit?
1	1 Benzene	2 Divinylbenzene	Fit
2	1 Benzene	3 alpha-Methyl styrene	Fit
3	1 Benzene	4 Naphthalene	Fit
4	1 Benzene	5 Styrene	Fit
5	1 Benzene	6 1-Phenylnaphthalene	Fit
6	1 Benzene	7 Biphenyl	Fit
7	1 Benzene	8 m-Terphenyl	Fit
8	1 Benzene	9 tert-Butylbenzene	Fit
9	1 Benzene	10 2-Phenyl-2,4,6-trimethylheptane	Fit

31 Benzene
59 Divinylbenzene

Fit Method
 Simplex Method by Nelder/Mead (SNM)
 SNM+Levenberg/Marquardt Method

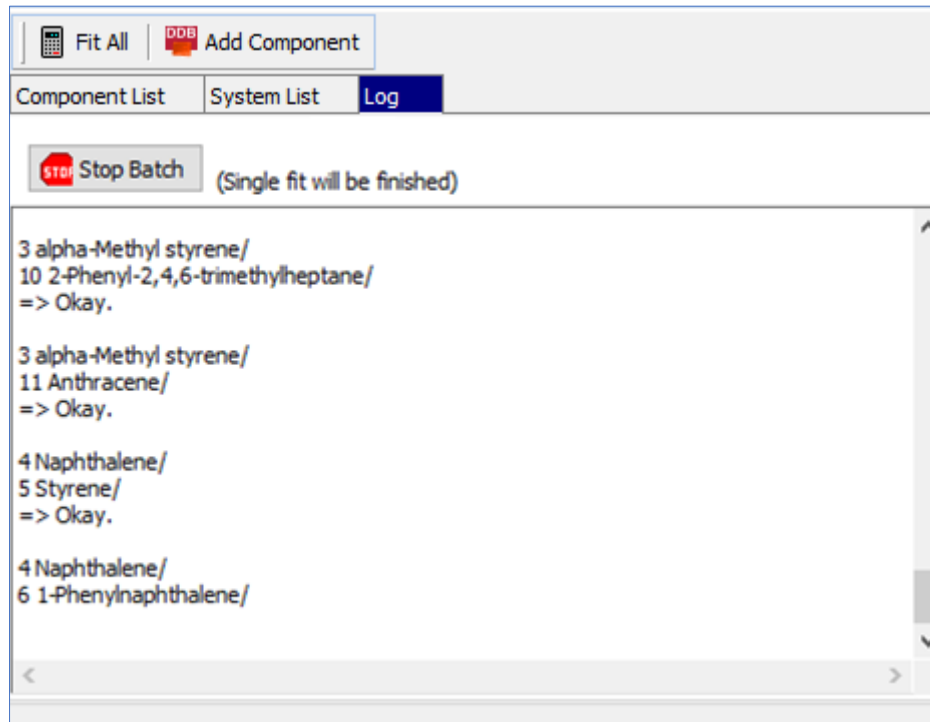
Figure 5: List of Systems

display both the list of components and the list of binary systems built from these components. The “Fit” button in a grid row will start a fit only for the single binary system displayed in the single

row. Whereas the “Fit All” button in the tool bar will start a batch fit for all the systems. This batch fit produces a protocol, which is displayed in the third page of this dialog. The method used for the fitting is chosen by the settings of the main menu.

The batch fit can be stopped by the corresponding button. A single fit will be finished before the batch stops. Any results from the already executed fits are saved in the “Result” windows (see next chapter) and are not lost.

The log window itself only stores information on the success of a fit or an error message if a fit cannot be performed due to, for example, missing group/group interaction parameters of a UNIFAC model.



5 Results

5.1 Recalculated Values

The recalculated values are shown alongside the source values in the data grid at the bottom of the dialog.

T [K]	x1	x2	Act.Coeff.1	Act.Coeff.2	Act.Coeff.1 gE Model	Act.Coeff.2 gE Model	Deviation1 [%]	Deviation2 [%]
300.00	0.0000	1.0000	2.0005	1.0000	2.0040	1.0000	-0.1727	0.0000
300.00	0.0005	0.9995	1.9994	1.0000	2.0023	1.0000	-0.1477	0.0000
300.00	0.0010	0.9990	1.9983	1.0000	2.0007	1.0000	-0.1228	0.0000
300.00	0.0015	0.9985	1.9972	1.0000	1.9991	1.0000	-0.0980	-0.0001

Figure 6: Result table

This table also shows the relative deviations.

This table can be saved as Excel file, copied to the Windows clipboard, and a diagram with the results can be shown.

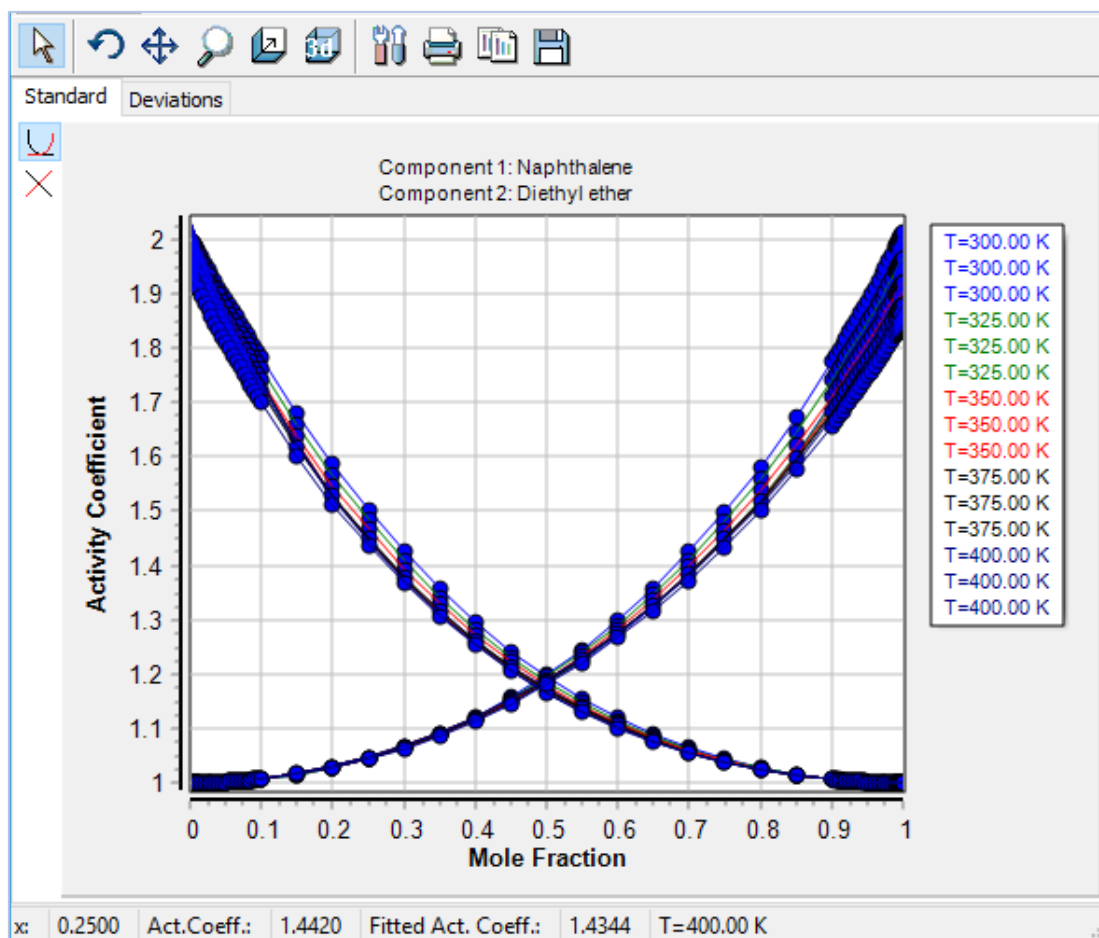


Figure 7: Result diagram

The diagram allows switching between a normal scale and a logarithmic scale, it can also be copied and saved, and a 3D display is possible.

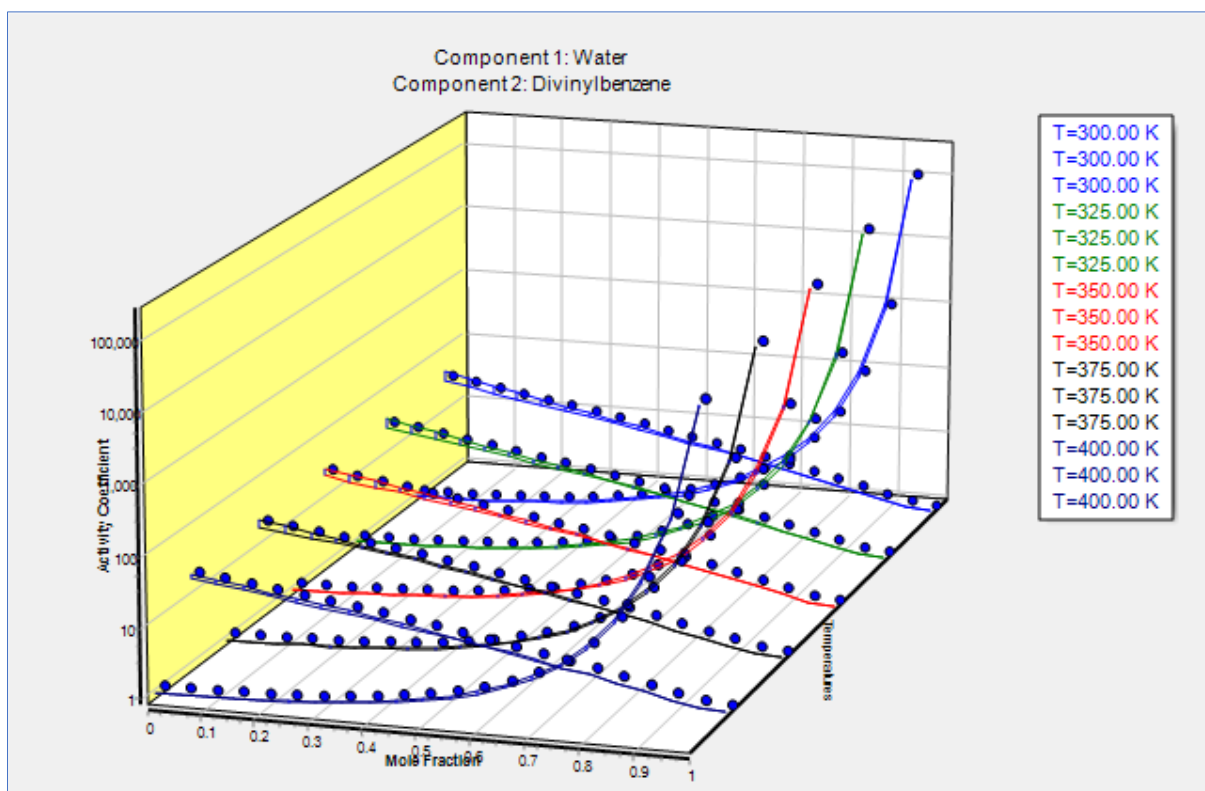


Figure 8: Result diagram 3D

5.2 Parameters

The obtained parameters are also displayed in a table. This table is used to collect all fit results.

DDB Results							
Save as XLS Save as INP Save in ParameterDDB Copy Clear							
63 Sets	a	b	c	d	e	f	a
Model	UNIQUAC		Set No. 63			Remove	
IA 1-2	293.30099	0	0	0	0	0	
IA 2-1	-199.59977	0	0	0	0	0	
Comp1	123 Naphthalene						
	r=4.9808	q=3.4400					
Comp2	12 Diethyl ether						
	r=3.3949	q=3.0160					
Obj. Function	AAD=0.0170996935 RMS=0.0301778152 MRD=0.940341389 %						
Aspen	a	b	c	d			
IA 1-2	0	-147.59438	0	0			
IA 2-1	0	100.44222	0	0			
Pro/II	a	b	c				

The parameters are given in [cal/mol], Aspen and PRO/II parameters in [K]

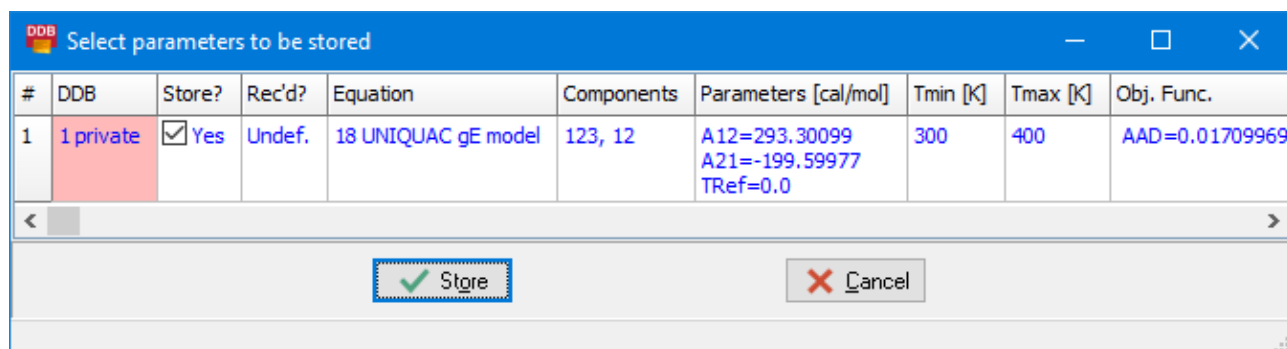
Figure 9: Fit Results Dialog

The parameters sets can be saved as Microsoft Excel file, as Aspen INP file, to the ParameterDDB,

and copied to the Windows clipboard.

The parameters saved in the Aspen INP file are fully Aspen compatible whereas all other locations store the parameters in a DDB software specific format. The ParameterDDB management software supports to copy g^E model parameters in the DDB format as well as in the Aspen format and the PRO/II format.

5.3 Save in the Parameter DDB



This export is displaying an additional selection dialog where all fitted parameter sets are listed. Single datasets can be included and excluded here before storing the entire list.

5.4 Save as Aspen INP Files

This export only needs the specification of a file name to create an INP file. This fit program is able to perform a match of the internal (DDB) components with the Aspen IDs and will write appropriate Aspen names in the INP file. If a match cannot be found a unique identifier is used which can be easily modified in Aspen.

6 Appendix

6.1 Conversion between DDB and Aspen Simulator Equations

6.1.1 Introduction

This section describes the different forms of the g^E model equations used in the Aspen simulator (short Aspen) and the Dortmund Data Bank (short DDB) for the three models Wilson, NRTL, and UNIQUAC. Wherever it is possible, a conversion of parameters is described.

6.1.2 Wilson

6.1.2.1 DDB Form

$$\ln y_i = -\ln \left(\sum_j x_j \Lambda_{ij} \right) + 1 - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}}$$

with

$$\Lambda_{ij} = \frac{v_j}{v_i} e^{-\Delta \lambda_{ij}/T}$$

v_i Molar volume of liquid pure component i at 25°C

$\Delta \lambda_{ij}$ are interaction parameters between component i and j [cal/mol] and can be made temperature-dependent:

$$\Delta \lambda_{ij} = a_{ij} + b_{ij} T + c_{ij} T^2 + d_{ij} T \cdot \ln T + e_{ij} T^3 + \frac{f_{ij}}{T}$$

6.1.2.2 Aspen Form

$$\ln y_i = 1 - \ln \left(\sum_j x_j \Lambda_{i,j} \right) - \frac{\sum_k x_k \Lambda_{k,j}}{\sum_j x_j \Lambda_{k,j}}$$

$$\Lambda_{i,j} = \exp \left(a_{i,j} + \frac{b_{i,j}}{T} + c_{i,j} \ln T + d_{i,j} T \right)$$

6.1.2.3 Conversion between DDB and Aspen Parameters

The Aspen form does not support the terms for e_{ij} and f_{ij} in the temperature-dependency of the interaction parameters. Therefore, parameter sets where e_{ij} or f_{ij} are non-zero cannot be converted to the Aspen equation.

On the other hand, Aspen incorporated the ratio of molar volumes at 25°C $\left(\frac{v_j}{v_i} \right)$ within the parameter $a_{i,j}$.

This makes it impossible to convert Aspen-style Wilson parameters into DDB parameters if any of the pure component Wilson volumes are missing.

The last difference is that DDB and Aspen are using different units for the interaction parameters – [cal/mol] in DDB and [K] in Aspen which leads to the conversion factor R (gas constant) in $\frac{\text{cal}}{\text{K}\cdot\text{mol}}$.

Aspen parameters	DDB parameters
$a_{i,j}$	$\ln\left(\frac{v_j}{v_i}\right) - \frac{b_{ij}}{R}$
$b_{i,j}$	$-\frac{a_{ij}}{R}$
$c_{i,j}$	$-\frac{d_{ij}}{R}$
$d_{i,j}$	$-\frac{c_{ij}}{R}$

$$R = 1.9872098 \frac{\text{cal}}{\text{K}\cdot\text{mol}}$$

6.1.3 NRTL

6.1.3.1 DDB Form

$$\ln y_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_n x_n \tau_{nj} G_{nj}}{\sum_k G_{kj} x_k} \right)$$

with

$$G_{i,j} = \exp(-\alpha_{ij} \tau_{ij})$$

and

$$\tau_{ij} = \frac{\Delta g_{ij}}{T}$$

Δg_{ij} are interaction parameters for component i and j [cal/mol]

$$\Delta g_{ij} = a_{ij} + b_{ij} T + c_{ij} T^2 + d_{ij} T \cdot \ln T + e_{ij} T^3 + \frac{f_{ij}}{T}$$

α_{ij} is the non-randomness parameter: $\alpha_{ij} = \alpha_{ji}$.

6.1.3.2 Aspen Form

$$\ln y_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_l x_l \tau_{lj} G_{lj}}{\sum_k G_{kj} x_k} \right)$$

with

$$G_{ji} = \exp(-S_{ji} \tau_{ji})$$

and

$$\tau_{ji} = a_{j,i} + \frac{b_{j,i}}{T} + e_{j,i} \ln T + f_{j,i} T$$

and

$$S_{ji} = c_{ji} + d_{ji}(T - 273.15) \quad (\text{non-randomness parameter})$$

6.1.3.3 Conversion between DDB and Aspen Forms

The conversion between DDB and Aspen parameters is mainly a conversion of units. DDB uses [cal/mol] and Aspen uses [K] which leads to the conversion factor R (gas constant) in $\frac{\text{cal}}{\text{K} \cdot \text{mol}}$.

DDB does not support a temperature-dependent non-randomness parameter which means that the Aspen parameter $d_{i,j}$ is always 0 and an Aspen parameter set including a temperature-dependency of the non-randomness parameter cannot be converted into DDB parameters.

The sequence of parameters is also slightly different.

Aspen parameters	DDB parameters
$a_{i,j}$	$\frac{b_{ij}}{R}$
$b_{i,j}$	$\frac{a_{ij}}{R}$
$c_{i,j}$	α_{ij}
$d_{i,j}$	0
$e_{i,j}$	$\frac{d_{ij}}{R}$
$f_{i,j}$	$\frac{c_{ij}}{R}$

$$R = 1.9872098 \frac{\text{cal}}{\text{K} \cdot \text{mol}}$$

6.1.4 UNIQUAC

6.1.4.1 DDB Form

$$\ln y_i = \ln y_i^C + \ln y_i^R$$

$$\ln y_i^C = 1 - V_i + \ln V_i - 5 q_i \left(1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i} \right)$$

$$\ln y_i^R = q_i \left(1 - \ln \frac{\sum_j q_j x_j \tau_{ji}}{\sum_j q_j x_j} - \sum_j \frac{q_j x_j \tau_{ij}}{\sum_k q_k x_k \tau_{kj}} \right)$$

with

$\ln y_i^C$ Combinatorial part of the activity coefficient of component i

$\ln y_i^R$ Residual part of the activity coefficient of component i

$\tau_{ij} = e^{-\Delta u_{ij}/T}$ Interaction parameters between component i and j [cal/mol]

$$\Delta u_{ij} = a_{ij} + b_{ij} T + c_{ij} T^2 + d_{ij} T \cdot \ln T + e_{ij} T^3 + \frac{f_{ij}}{T}$$

$$V_i = \frac{r_i}{\sum_j r_j x_j} \quad \text{Volume fraction}$$

$$F_i = \frac{q_i}{\sum_j q_j x_j} \quad \text{Surface fraction}$$

r_i Relative van der Waals volume of component i

q_i Relative van der Waals surface of component i

6.1.4.2 Aspen Form

The activity coefficient is calculated from a residual and a combinatorial part.

$$\ln y_i = \ln y_i^C + \ln y_i^R$$

The combinatorial part is determined by

$$\ln y_i^C = \ln \frac{V_i}{x_i} + \frac{z}{2} q_i \ln \frac{F_i}{V_i} + l_i - \frac{V_i}{x_i} \sum_j x_j l_j$$

The coordination number is $z = 10$.

The residual part is determined by

$$\ln y_i^R = q_i \left(1 - \ln \sum_j F_j \tau_{j,i} - \sum_j \frac{F_j \tau_{i,j}}{\sum_k F_k \tau_{k,j}} \right) \quad \text{or} \quad \ln y_i^R = q'_i \left(1 - \ln \sum_j F'_j \tau_{j,i} - \sum_j \frac{F'_j \tau_{i,j}}{\sum_k F'_k \tau_{k,j}} \right)$$

with

$$l_i = 5(r_i - q_i) - (r_i - 1)$$

$$V_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad \text{Volume fraction}$$

$$F_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad \text{or} \quad F'_i = \frac{q'_i x_i}{\sum_j q'_j x_j} \quad \text{Surface fraction, the F' version is used for alcohols and Water.}$$

$$\tau_{j,i} = \exp\left(a_{j,i} + \frac{b_{j,i}}{T} + c_{j,i} \ln T + d_{j,i} T\right)$$

6.1.4.3 Conversion between DDB and Aspen Form

The conversion between DDB and Aspen parameters is mainly a conversion of units. DDB uses [cal/mol] and Aspen uses [K] which leads to the conversion factor R (gas constant) in $\frac{\text{cal}}{\text{K}\cdot\text{mol}}$.

There is one bigger difference regarding alcohols and Water containing mixtures. Aspen uses a slightly different equation form for alcohols and Water mainly caused by a different relative van der Waals surface constant (q') making it impossible to convert DDB parameters into Aspen parameters if these components are encountered.

Aspen parameters	DDB parameters
$a_{i,j}$	$-\frac{b_{ij}}{R}$
$b_{i,j}$	$-\frac{a_{ij}}{R}$
$c_{i,j}$	$-\frac{d_{ij}}{R}$
$d_{i,j}$	$-\frac{c_{ij}}{R}$

$$R = 1.9872098 \frac{\text{cal}}{\text{K}\cdot\text{mol}}$$