

Fit of g^E Model Parameters to Activity Coefficients Obtained from Group Contribution Methods

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

DDBSP - Dortmund Data Bank Software Package



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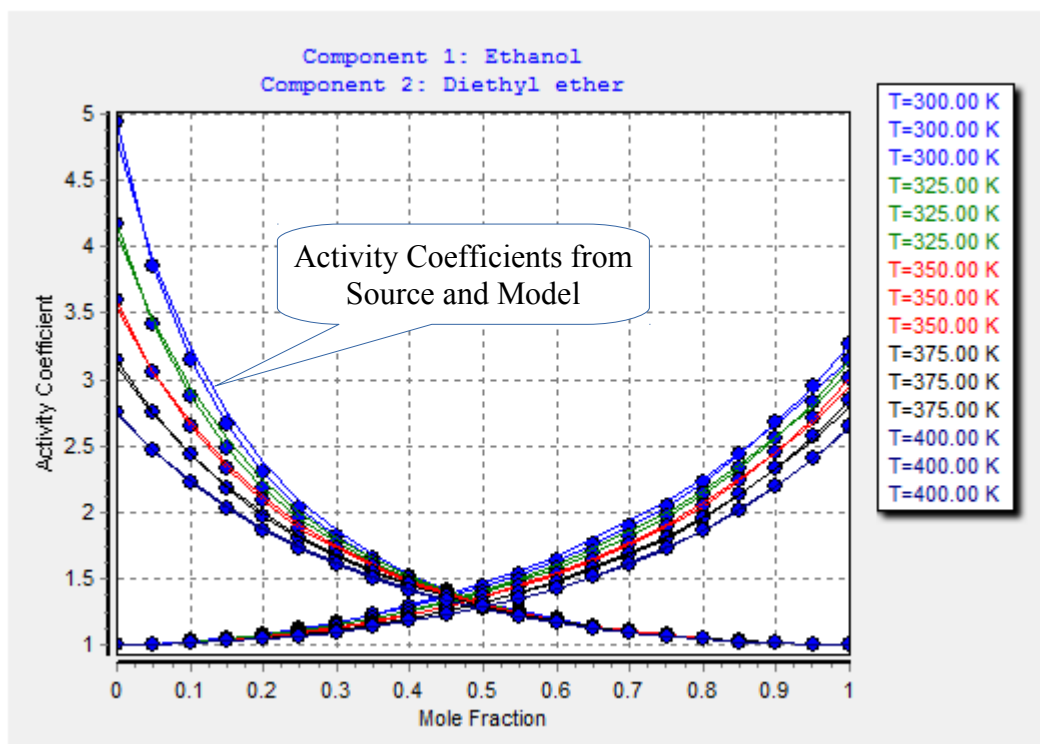
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Introduction

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), NIST-modified UNIFAC, and ASOG for binary systems.

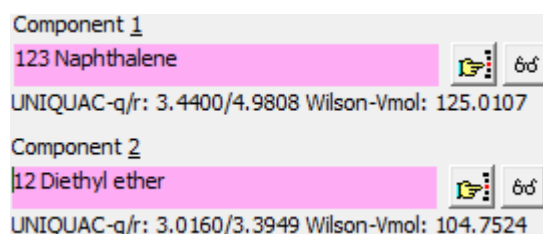
This software can obtain parameters for a high number of systems in a short time. These parameters have the same quality as the underlying activity coefficient model, the program neither adds or loses quality. There's still a slight degradation of precision because of a remaining fit deviation.



This deviation normally doesn't 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.

Component Selection



This part of the main dialog allows to specify the two components of the binary systems either the standard component selection dialog or by typing a known DDB component number.

11| | → Press Return → 11 Ethanol|

The program displays some data relevant data for the g^E models

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

If any of these values are 0 the corresponding model cannot be used.

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

Component 2
12 Diethyl ether
UNIQUAC-q/r: 3.0160/3.3949 Wilson-Vmol: 104.7524

Component 1
15987 3-Chloro-2-ethynyl-tetrahydrofuran
UNIQUAC-q/r: 3.5880/4.5696 Wilson-Vmol: 0.0000

Density: 778.00 kg/m³ at

UNIQUAC Groups and UNIQUAC Parameters

UNIQUAC Groups: 2 1001 1020

mod. UNIQUAC Groups: 2 1001 1020 0 0 0 0 0

UNIQUAC r-value: 1.89910 UNIQUAC q-value: 1.79600

Wilson volume is calculated from this density

UNIQUAC surface and volume

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

Component 1
11 Ethanol
UNIQUAC-q/r: 1.9720/2.1055 Wilson-Vmol: 58.6867

Component 2
12 Diethyl ether
UNIQUAC-q/r: 3.0160/3.3949 Wilson-Vmol: 104.7524

Component Details: Diethyl ether

UNIQUAC-r 3.3949

UNIQUAC-q 3.0160

V Wilson 104.7524

UNIFAC groups

3	2 times 1 CH3 [CH2]	1 time 2 CH2 [CH2]	1 time 25 CH2O [CH2O]
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mod. UNIFAC (Dortmund) groups

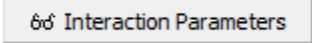
3	1 time 2 CH2 [CH2]	2 times 1 CH3 [CH2]	1 time 25 CH2O [CH2O]
---	--------------------	---------------------	-----------------------

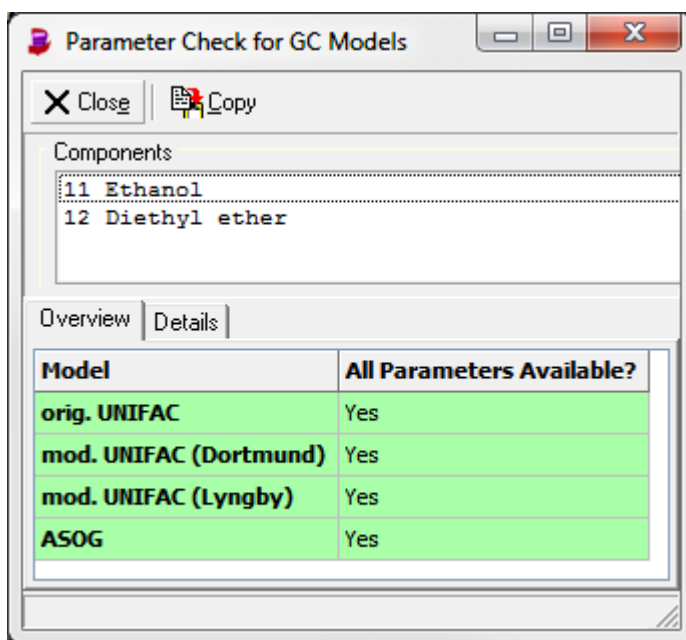
mod. UNIFAC (Lyngby) groups

3	2 times 1 CH3 [CH2]	1 time 2 CH2 [CH2]	1 time 21 CH2O [CH2O]
---	---------------------	--------------------	-----------------------

ASOG groups

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

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

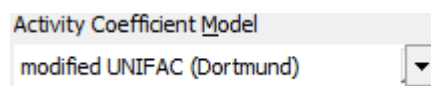


Green lines indicate that this model can be used to calculate activity coefficients – group assignment and interaction parameters are available. Red lines indicate either a missing group assignment or missing interaction parameters. The “Details” page allows to identify the problem.

Calculating Activity Coefficients

Four different models are currently available for the calculation of activity coefficients:

- original UNIFAC
- modified UNIFAC (Dortmund)
- modified UNIFAC (Lyngby)
- ASOG
- COSMO-RS (OI)
- COSMO-SAC




The first two models are maintained by the UNIFAC consortium (www.unifac.org). 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: 300, End: 400, Step: 25
 Mole Percent Step Width: 5
 Enhanced Resolution for Small Concentrations

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  has to be used to force the program to recalculate the activity coefficient table.

Fitting

The program allows to fit parameters for the g^E models UNIQUAC, NRTL, and Wilson.

gE Model
 NRTL

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

$$a_{ij} + b_{ij} * T + c_{ij} * T^2 + d_{ij} * T * \ln(T) + e_{ij} * T^3 + \frac{f_{ij}}{T}$$

All parameters can be switched on and off.

Temperature Dependency
 aij, dij*T*ln(T)
 bij*T, eij*T^3
 cij*T^2, fij/T
 Quick Select: Aspen

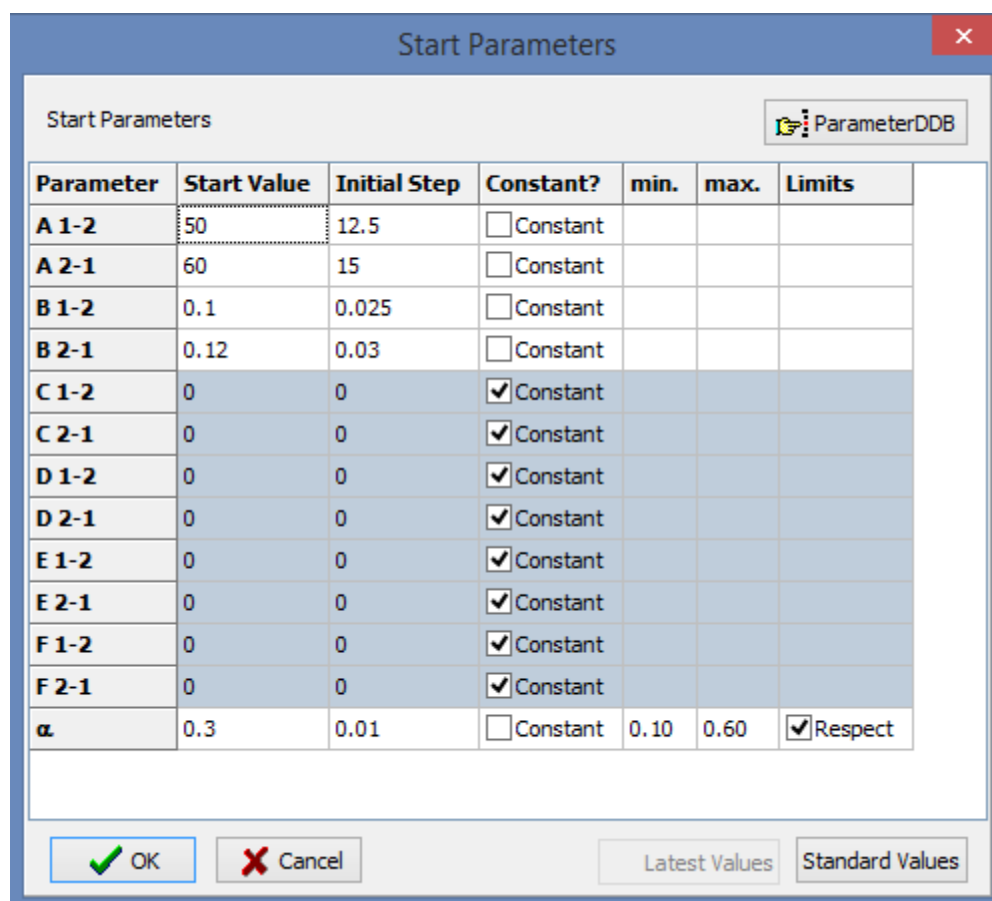
The “Quick Select” combobox

Quick Select
 DDB Quadratic Temperature-Dependent
 DDB Temperature-Independent
 DDB Linear Temperature-Dependent
 DDB Quadratic Temperature-Dependent
 Pro/II
 Aspen

defines some short cuts to often used parameter sets.

Starting Values

Starting values for the parameters can be modified by  :



The grid is editable and allows to enter starting values 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. Unchecking this control will bring back the previously entered step width.

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.

Objective Function



The objective function can be set to

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

All three objective function have different advantages and downsides.


Loops



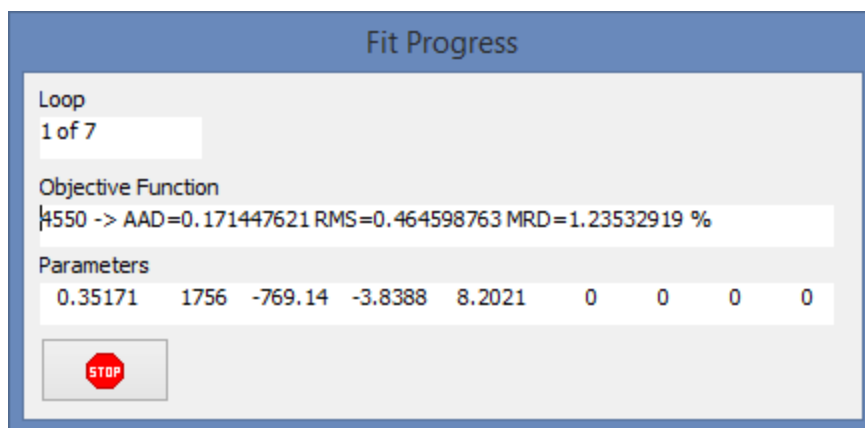
The “Loops” setting is used to restart the fit procedure up to four times. This is a useful and often necessary feature because the changes in the objective function are rather small near the minimum and the optimization process is starving before reaching a *global* minimum. The re-start uses the obtained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

Fitting

The  button starts the fit. The used algorithm is Simplex-Nelder-Mead (SNM). This 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.

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



The  button allows stopping the current fit process.

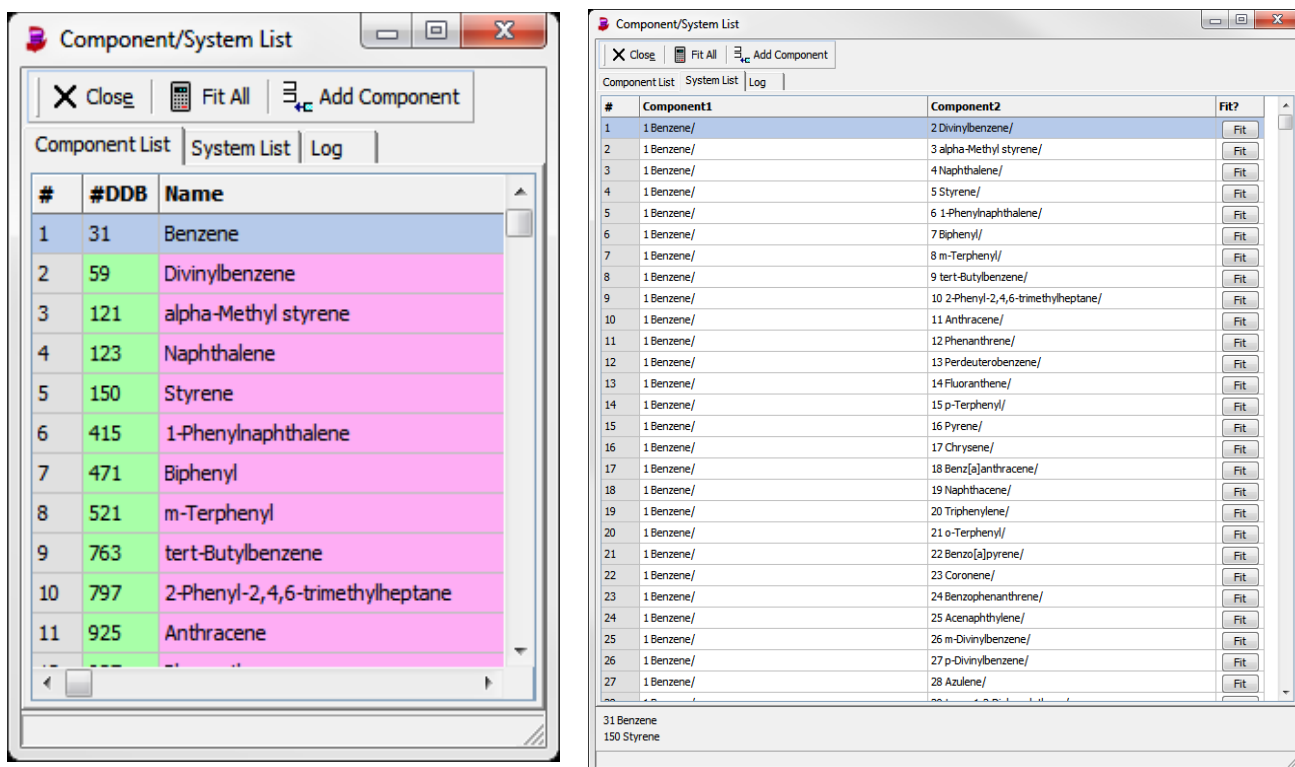
The sequence of the parameters are always



- 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} (quadratically temperature-dependent parameter)
- and so on

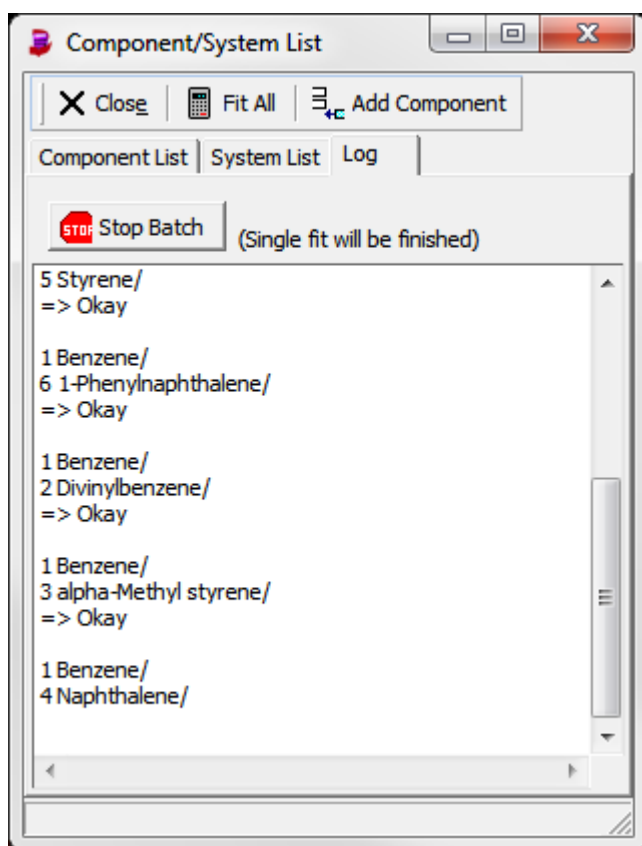
Batch Fitting

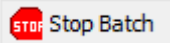
The program allows to fit multiple systems in a row. These systems will be build from component lists which can be created by other DDB software like the component management program, the Artist structure editor, or the DDB main retrieval program.

The dialogs



display both the list of components and the list of binary systems built from these components. The  button in the single grid rows will start a fit only for the single binary system displayed in the single row whereas the  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 batch fit can be stopped by the  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 can't be performed due to, for example, missing group/group interaction parameters of a UNIFAC model.

Results

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

1 Set	a	b	c	d	e	f	α
Model	NRTL		Set No. 1			Remove	
IA 1-2	1756.0355	-3.8390646	0.0000000	0.0000000	0.0000000	0.0000000	0.3517001
IA 2-1	-769.23933	8.2023645	0.0000000	0.0000000	0.0000000	0.0000000	0.3517001
Comp1	40 2-Butanone						
	r=3.2479	q=2.8760	vmol=90.17				
Comp2	174 Water						
	r=0.9200	q=1.4000	vmol=18.07				
Obj. Function	AAD=0.171447541 RMS=0.464575584 MRD=1.2353876 %						
Aspen	a	b	c	d	e	f	
IA 1-2	-1.9318869	883.6689	0.3517001	0	0	0	
IA 2-1	4.1275785	-387.09518	0.3517001	0	0	0	

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

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.

Save in ParameterDDB

#	DDB	Store?	Rec'd?	Equation	Components	Parameters	Tmin	Tmax	Obj. Func.	
1	1 private	<input checked="" type="checkbox"/>	Yes	Undef.	17 NRTL gE model	40, 174	A12=1756.0355 A21=-769.23933 B12=-3.8390646 B21=8.2023645 Alpha=0.3517001 TRef=0.	300	400	AAD=0.171447541 RMS=0.46457558

Context Menu: Select All, Select None, Swap Selection

Buttons: Store, Cancel

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.

This ParameterDDB is also used to export parameters in various other formats.

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 can't be found a unique identifier is used which can be easily modified in Aspen.

Import Aspen Components

This feature allows to import components from Aspen simulator files. Supported files are the INP, the BKP, and the APT files.

This fit program will not only load the component identifiers but it also loads group assignments which will be matched automatically to DDB group assignments.

After a fit has been performed the program will write an INP file with the appropriate Aspen component identifiers allowing to seamlessly import the fitted g^E model parameters.

The UNIFAC Consortium

This program fully supports the parameter files developed by the UNIFAC consortium (www.unifac.org).