

Calculate X3

Calculation of Ternary Phase Equilibrium Diagrams



DDBST

Dortmund Data Bank
Software & Separation
Technology

DDBST - Dortmund Data Bank Software & Separation Technology GmbH

Marie-Curie-Straße 10

D-26129 Oldenburg

Tel.: +49 441 36 18 19 0

support@ddbst.com

www.ddbst.com

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1 Introduction

Vapor-liquid and solid-liquid phase equilibria as well as mixing enthalpies for ternary systems are quite difficult to visualize in an easily comprehensible manor. The program DDB CalculateX3 has been implemented to solve this problem and deliver insight in the phase behavior of ternary systems.

DDB CalculateX3 uses the activity coefficient models UNIFAC^{1,2,3,4,5}, modified UNIFAC (Dortmund)^{6,7,8,9,10} and NIST-mod. UNIFAC¹¹ and the group contribution equations of state PSRK¹² and VTPR^{13,14} to estimate the phase equilibria and mixing enthalpies. It also uses COSMO methods like COSMO-RS(OI)¹⁵, COSMO-SAC¹⁶, COSMO-SAC 2010¹⁷ and COSMO-SAC 2013¹⁸ (see next page for all models supported).

The application is part of the *Predictive Methods* add-on for the *DDB Access Package*.

2 Overview

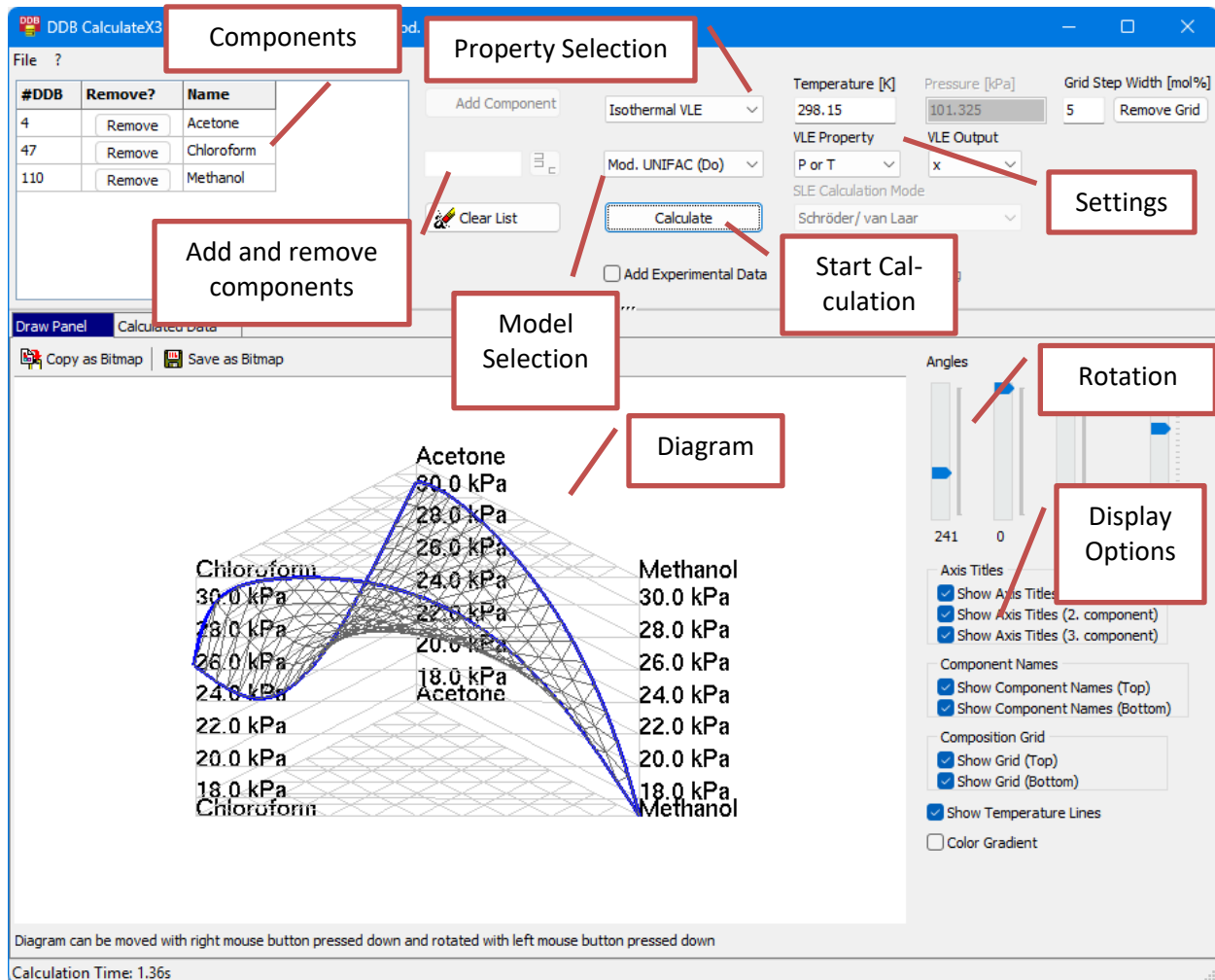


Figure 1: Main window.

2.1 Component Selection

The program allows the selection of three components either by DDB Components using the “Add Component” button or by typing the DDB component numbers directly in the edit field.

#DDB	Remove?	Name
4	<input type="button" value="Remove"/>	Acetone
47	<input type="button" value="Remove"/>	Chloroform
110	<input type="button" value="Remove"/>	Methanol

#DDB	Remove?	Name
47	<input type="button" value="Remove"/>	Chloroform
4	<input type="button" value="Remove"/>	Acetone
110	<input type="button" value="Remove"/>	Methanol

Single components can be removed by selecting the “Remove” button of its line. The complete list can be removed by selecting the button “Clear List“. The components can be sorted with the mouse by dragging a component to another line.

3 Calculation

First, the target property (SLE, h^E , isothermal or isobaric VLE, γ , and activity coefficient) has to be selected. Then the calculation can be started using the “Calculate” button. The SLE calculation is the slowest because the program has to iterate a lot especially for finding the binary eutectic points and the ternary eutectic lines.

3.1 Activity Coefficient Models

Currently the following models are supported:

- NRTL
- UNIQUAC
- Wilson
- original UNIFAC
- UNIFAC 2.0
- modified UNIFAC (Dortmund)
- Modified UNIFAC 2.0
- NIST modified UNIFAC
- PSRK
- PSRK 2.0
- VTPR
- COSMO-RS(OI)
- COSMO-SAC
- COSMO-SAC 2010
- COSMO-SAC 2013
- TUC 23 – UNIFAC
- TUC 23 – Mod. UNIFAC (Do.)
- TUC 23 – Mod. UNIFAC COSMO
- TUC 23 – PSRK UNIFAC
- TUC 23 – VTPR
- TUC 24 – UNIFAC
- TUC 24 – Mod. UNIFAC (Do.)
- TUC 24 – Mod. UNIFAC COSMO
- TUC 24 – PSRK UNIFAC
- TUC 24 – VTPR

4 Calculation Settings

Figure 2: Calculation settings.

4.1 Temperature

The temperature setting is only used for h^E , isothermal VLE, γ , and activity calculations because the temperature is the SLE calculation result.

4.2 Pressure

The pressure is used for isobaric VLE calculations and for heat of mixing and activity (coefficient) calculations with EOS models.

4.3 Calculation Step Width

The “Grid Step Width” determines the resolution of the calculation grid. The smaller the step width is set the better the result will be – but the screen resolution limit will make results in very high resolutions looking strange.

4.4 SLE Calculation Mode

It is possible to choose between the equation by Schröder/van Laar and by Neau.

$$\text{Neau:} \quad \ln x_i = -\ln \gamma_i - \Delta_{fus} \frac{H}{RT_M} \ln \left(\frac{T_M}{T} \right)$$

$$\text{Schröder/van Laar:} \quad \ln x_i = -\ln \gamma_i - \Delta_{fus} \frac{H}{R} \left(\frac{1}{T} - \frac{1}{T_M} \right)$$

4.5 Adding Experimental Data

It is possible to add experimental data if VLE, HE, ACT, or SLE data banks are available. The experimental data are displayed as small boxes.

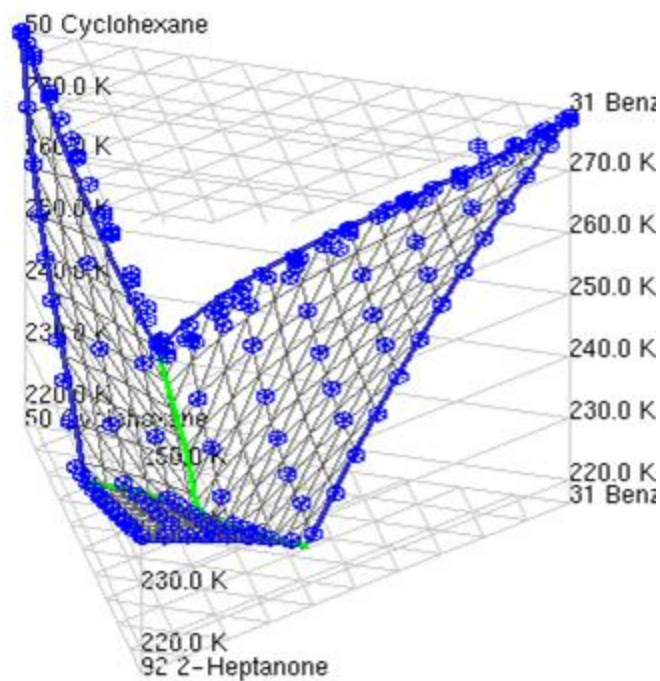


Figure 3: Added experimental data

If multiple **VLE** data sets with matching (constant temperature or pressure) experimental data exist, then a selection dialog allows the user to include or exclude single data sets.

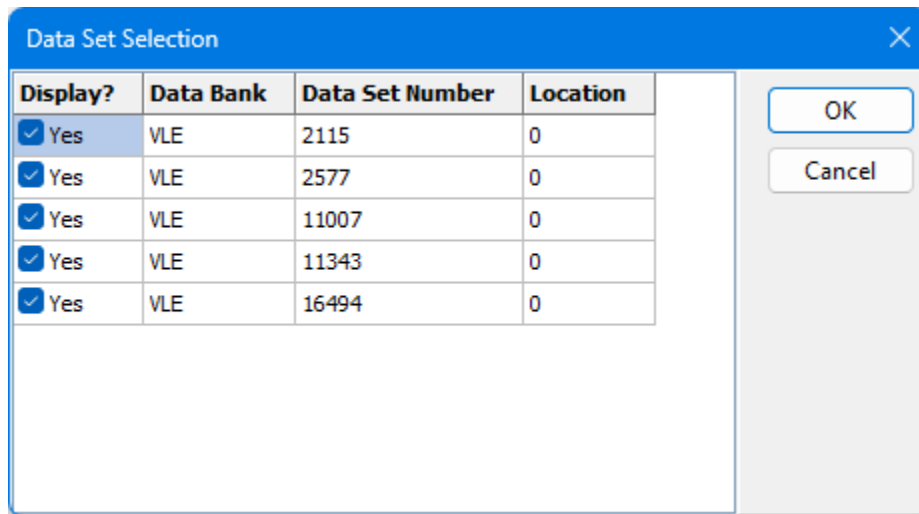


Figure 4: Data set selection.

4.6 VLE Output

As *VLE property*, the user can select one of the following options:

- the standard pressure or temperature planes (P for isothermal calculations, T for isobaric)
- a deviation diagram of the absolute differences between liquid and vapor composition
- the display of K factors
- the fraction between K factors (separation factor)

The *VLE output* setting determines whether the liquid or the vapor composition or both should be used.

5 Calculated Data

The program calculates the entire component range from 0 to 1 for all components with the specified step size. The raw data are displayed in a table.

#	x1 [mol/mol]	x2 [mol/mol]	x3 [mol/mol]	Tm [K]
7	0.0000	0.0600	0.9400	169.8553
8	0.0000	0.0700	0.9300	168.8569
9	0.0000	0.0800	0.9200	167.8330
10	0.0000	0.0900	0.9100	166.7847

Figure 5: Calculated data.

The data table can be copied to the Windows clipboard.

5.1 Typical Results

5.1.1 Solid-Liquid Equilibria

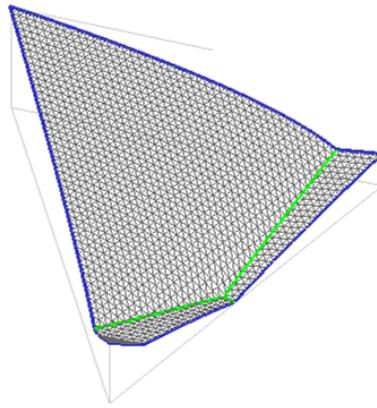


Figure 6: *m*-xylene – *p*-xylene - tetrachloromethane

Figure 6 shows a typical result where all labels and legends have been omitted. The mole fractions (resolution 2 mole-%) of the three components are displayed as a triangle as used typically in liquid-liquid equilibrium diagrams. The heights of the lines are the melting points of the mixture at the given composition.

The blue lines are the binary SLE curves and the green lines are the eutectic curves for the ternary system. All three blue lines have minimums representing the eutectic point of the binary system. The three green lines start from the binary eutectic points and meet each other in the eutectic point of the ternary system representing normally the lowest melting point. The gray net represents the melting points of the mixture at the given composition.

5.1.1.1 SLE Eutectic Lines

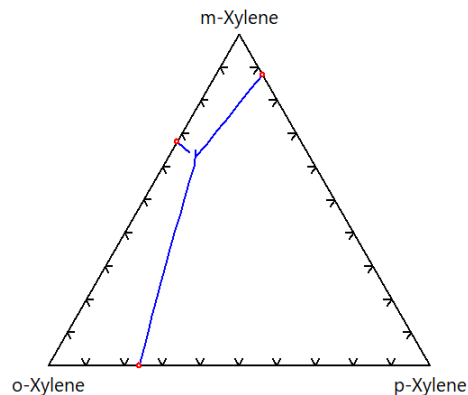


Figure 7: Eutectic lines.

This diagram is a projection of the 3D diagram to the 2D plane. It shows the eutectic lines only in a Gibbs' triangle.

5.1.2 Vapor-Liquid Equilibria

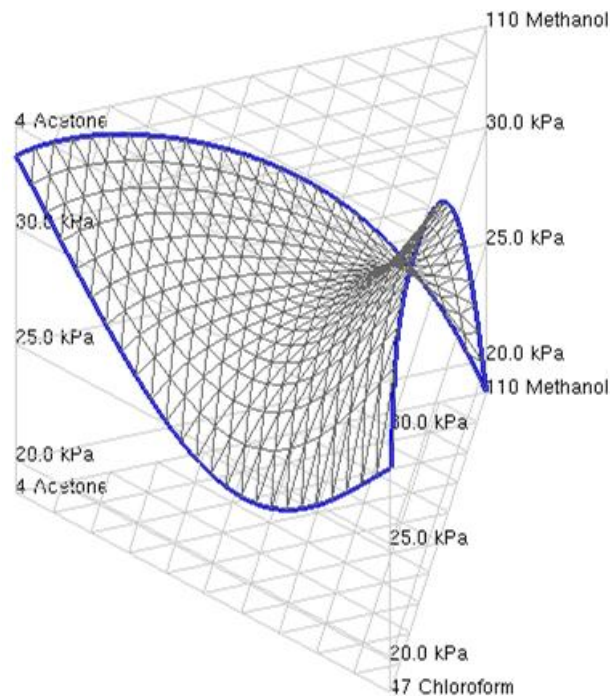


Figure 8: Methanol – acetone - chloroform

Figure 8 shows a not so typical result for a system building azeotropes in both the binary and ternary area. This is an example for a saddle-point azeotrope and it can be easily seen from the diagram why this name has been chosen. In these diagrams all labels and legends are shown and the resolution is 5 mole-%. Acetone and chloroform form a pressure minimum azeotrope, whereas chloroform and methanol as well as acetone and methanol form a pressure maximum azeotrope.

The deviation diagram (deviation between vapor and liquid compositions)

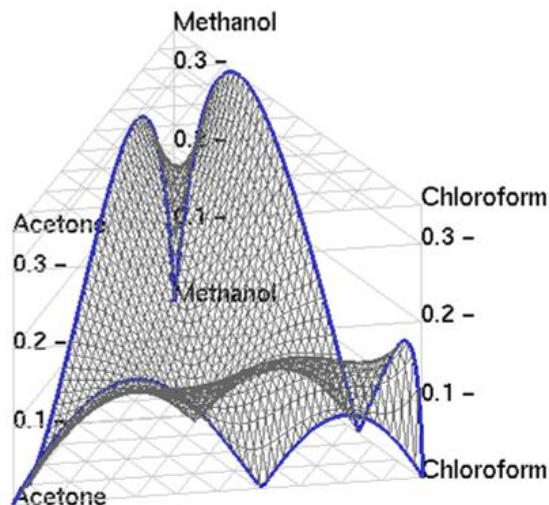


Figure 9: Deviation diagram.

shows the azeotropic point as 0 values touching the bottom.

If both vapor and liquid composition are selected, two planes are shown.

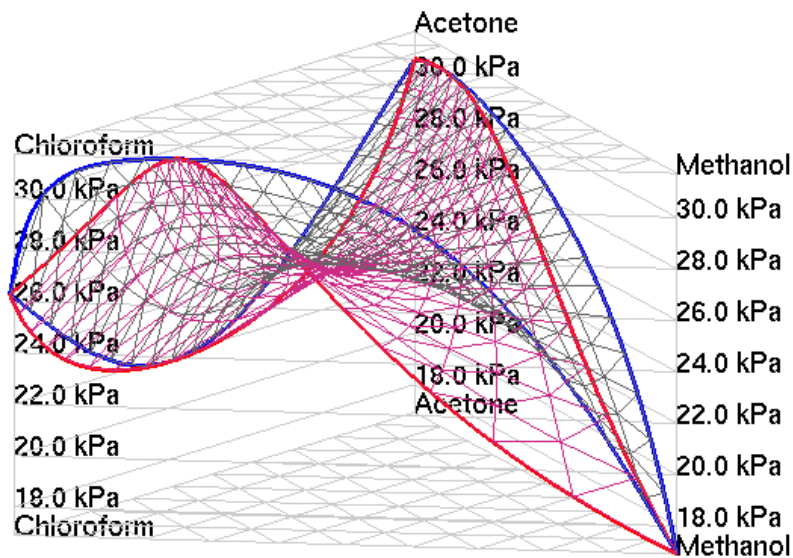


Figure 10: Vapor and liquid composition planes.

5.1.3 Excess enthalpies

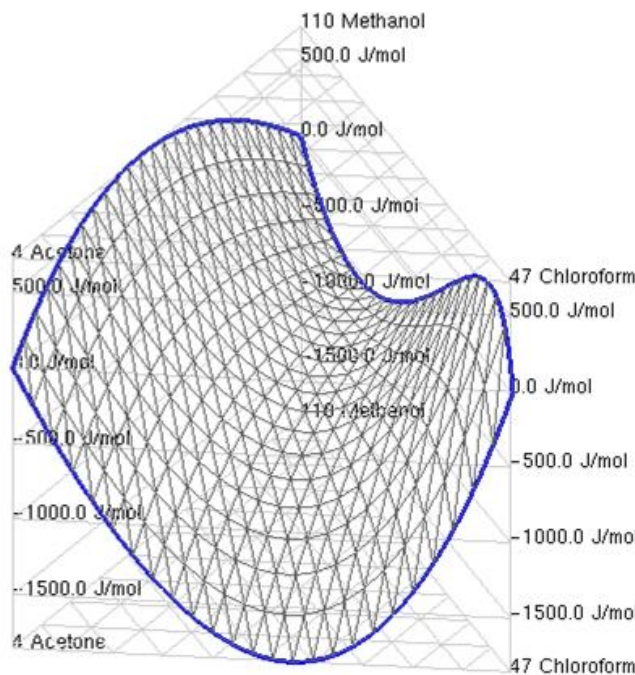


Figure 11: Excess enthalpies of the system methanol – acetone – chloroform.

Figure 11 shows the same system as already used for the VLE calculation. The blue lines are the excess enthalpies of the binary systems. The binary system acetone - chloroform has strong negative excess enthalpies. A negative value denotes that mixing is exothermic.

The excess enthalpies of the system methanol - acetone are strong positive. This positive value indicates that mixing is endothermic. The h^E has a quite similar shape as the VLE diagram but it does not build a saddle.

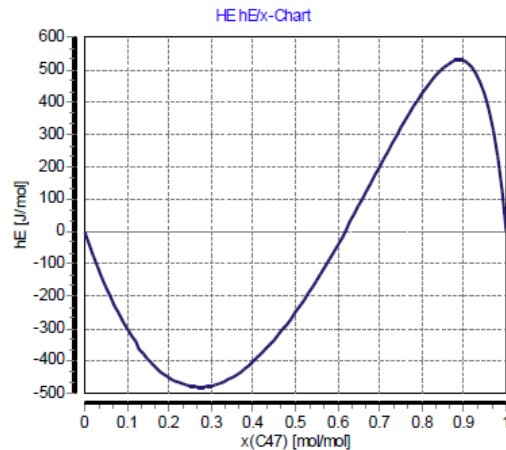


Figure 12: Excess enthalpies of the system Chloroform – methanol.

The system Chloroform/Methanol has both a positive and a negative excess enthalpy depending on the composition of the mixture.

5.1.4 Activity Coefficients

The activity coefficient calculation needs one further setting. It has to be determined for which component the γ shall be shown.

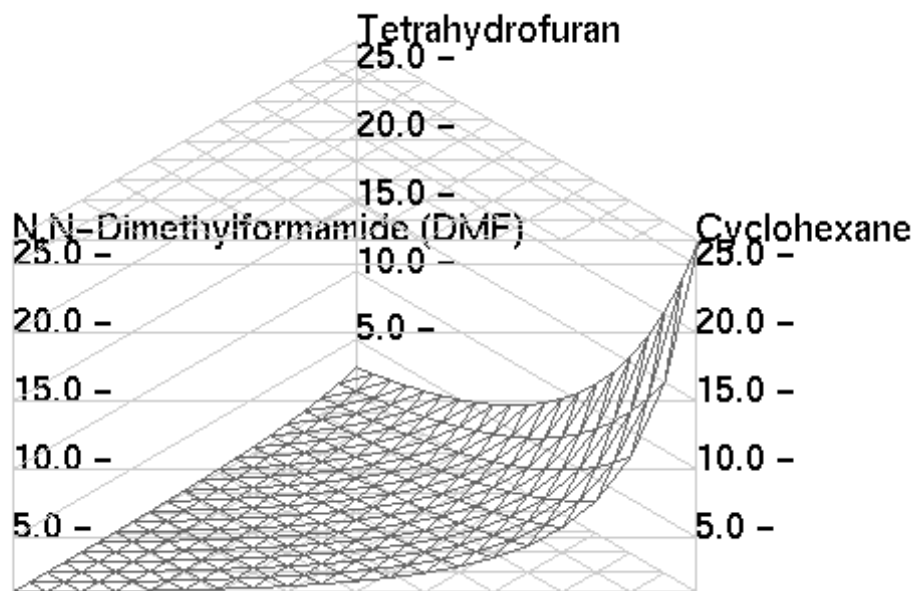


Figure 13: System DMF – THF – cyclohexane.

Figure 13 shows the activity coefficient plane N,N-dimethylformamide in the ternary system cyclohexane + tetrahydrofurane + N,N-dimethylformamide. In this calculation, only the calculated net for the complete compositions is shown and the binary lines are not emphasized.

The diagram with all three activity coefficients looks like this:

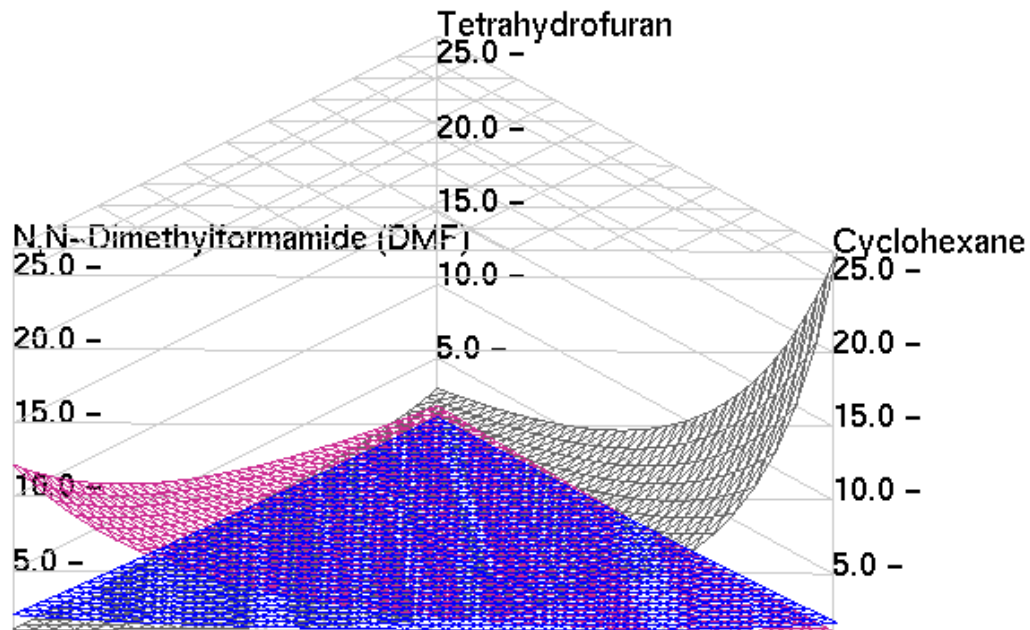


Figure 14: Activity coefficients for the ternary system DMF – THF – cyclohexane.

5.1.5 Activities

Activities are defined as $a_i = x_i * \gamma_i$. The activity calculation has also one further setting. It has to be determined for which component the activity shall be shown.

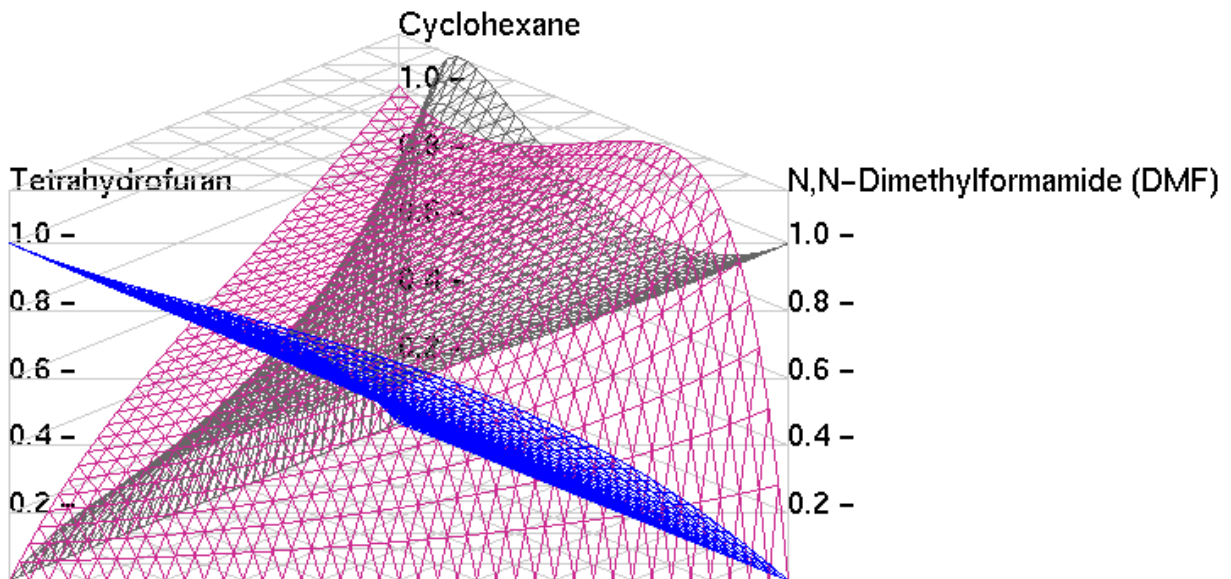


Figure 15: Activities for the ternary system DMS – THF – cyclohexane.

5.2 Rotating and sizing the diagram

Rotating can also be done directly by the mouse. If the mouse is moved over the diagram – and the left mouse key is pressed down – the diagram will be rotated around the x-axis when the mouse cursor is moved up and down, and around the y-axis when the mouse cursor is moved to the left or right.

With the right key pressed down the chart can be moved. The check boxes below the sliders allow switching on and off labels and legends in the diagram.

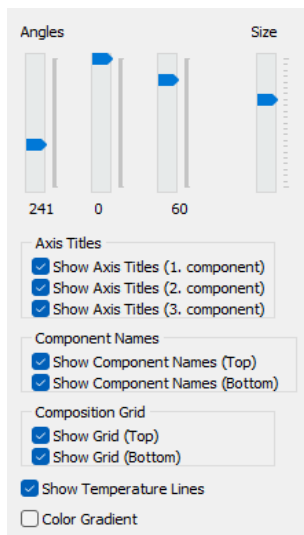


Figure 16: Rotating and sizing options.

The three sliders below the “Angles” title on this panel sitting at the right side of the diagram also allow rotating the diagram in all three directions in space. The “Size” slider enlarges or reduces the size of the diagram.

Color gradient replaces the normal single color by a gradient from blue for low values to red for high values. A typical example is this:

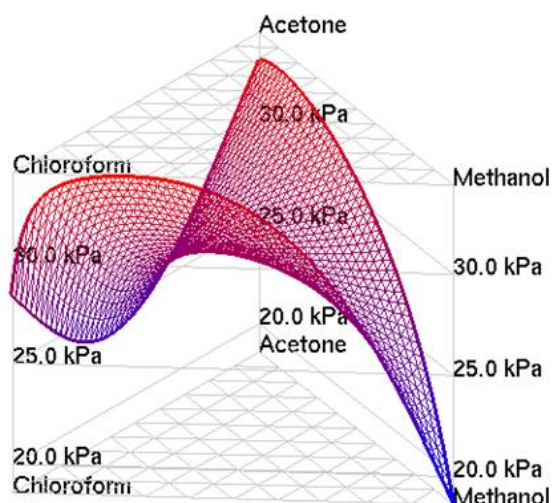


Figure 17: Color gradients.

5.3 Copying and saving the diagram

The diagram can be copied to the clipboard using the tool bar button “Copy as bitmap”. The button “Save as bitmap” saves the diagram to a file.

6 Limitations

6.1 Solid-Liquid Equilibria

Only eutectic systems can be calculated correctly. A prerequisite for the calculation is the availability of the melting temperature (T_m) and the melting enthalpy (H_m) for every single component. T_m and H_m are both taken from the DDB basic component file.

6.2 Vapor-Liquid Equilibria

The vapor phase is calculated ideally and no test on liquid-liquid equilibrium is performed. If the vapor phase is strongly non-ideal or if miscibility gaps are present, the calculation will give wrong results.

The calculation needs the saturated vapor pressures for all pure components. The parameters are calculated with the Antoine equation for which the parameters are taken from the Parameter DDB, a part of the Dortmund Data Bank.

6.3 Models

Some models are group contribution methods. The calculation needs the list of groups for every component, which is taken from the DDB basic component file. The model specific group interaction parameters are provided through a DDB specific parameter file.

This parameter file and the list of groups exist in two versions. There's a relatively small list of groups and parameters which have been published in the freely accessible literature and there's an extended list of groups and parameters provided by the UNIFAC consortium (<http://www.unifac.org/>). This – by the factor of two – extended list is only available for members of that consortium. The consortium list contains not only many new parameters for new groups but also a lot of revised parameters.

Four models are COSMO methods which need a sigma profile for every component.

7 Literature

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 - ¹⁶ Lin S.-T., Sandler S.I., "A Priori Phase Equilibrium Prediction from a Segment Contribution Solvation Model", *Ind.Eng.Chem.Res.*, 2002, 41(5), 899-913
 - ¹⁷ Hsieh C.-M., Sandler S.I., Lin S.-T., "Improvements of COSMO-SAC for vapor-liquid and liquid-liquid equilibrium predictions", *Fluid Phase Equilib.*, 2010, 297(1), 90-97
 - ¹⁸ Hsieh C.-M., Lin S.-T., Vrabec J., "Considering the dispersive interactions in the COSMO-SAC model for more accurate predictions of fluid phase behavior", *Fluid Phase Equilib.*, 2014, 367, 109-116