ENTRAINER SELECTION

Calculation of Additives and Separation Methods

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1. Introduction

Although conventional distillation is the most important industrial separation process, there are situations where solvent-enhanced separation, e. g. azeotropic distillation, extractive distillation, liquid-liquid extraction, and absorption is a more appropriate choice. Therefore a software package was developed in order to find a suitable solvent (entrainer) for the above mentioned separation processes. The entrainer selection is based on azeotropic data, activity coefficients at infinite dilution and liquid-liquid equilibrium (LLE) data. These data are taken from factual data banks as well as from thermodynamic models.

The program starts with an Entrainer Preselection page.
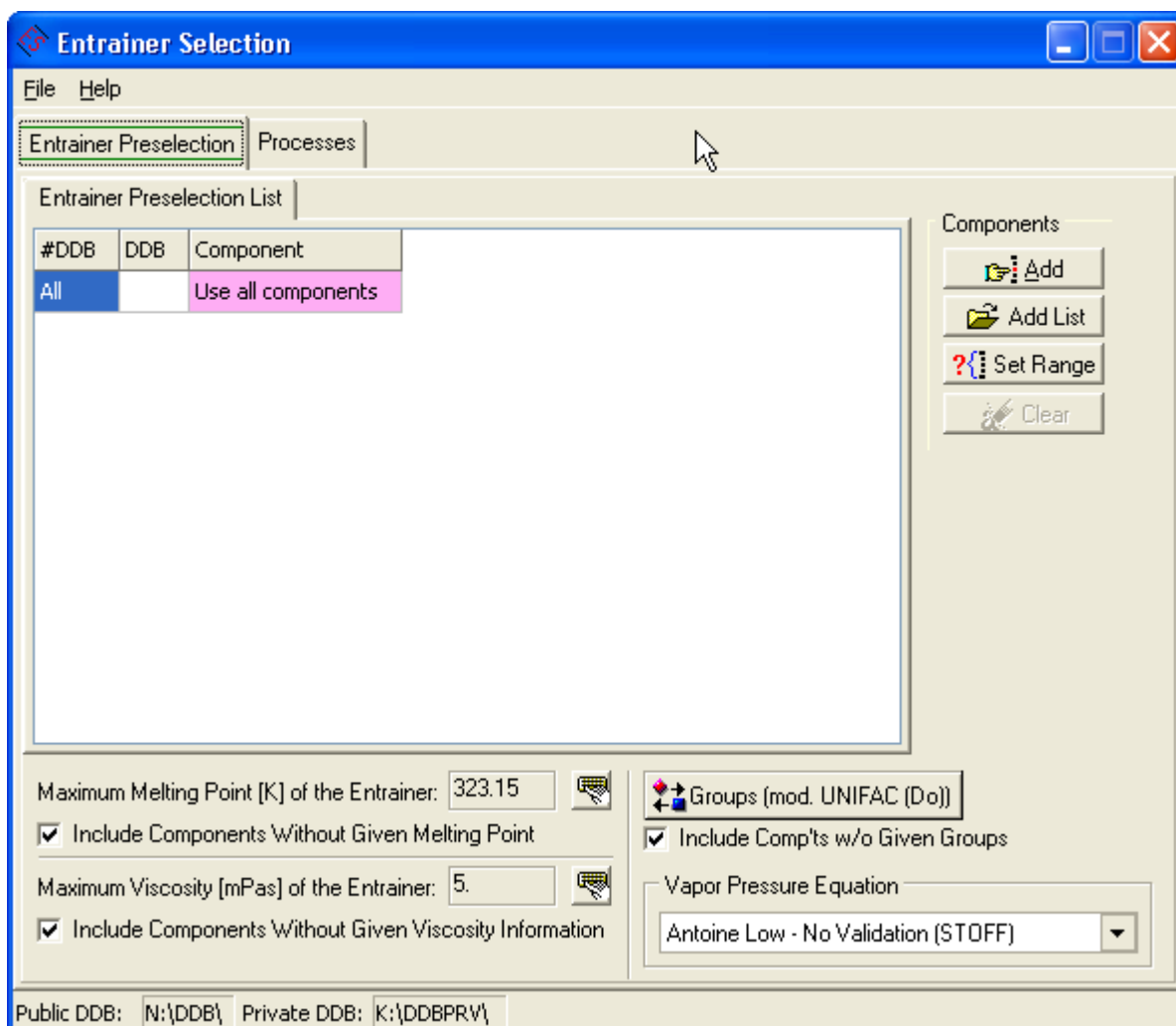
The dialog offers the possibility to specify the component range. This is useful, if the azeotropic data are calculated with a thermodynamic model. Instead of calculating the homogeneous and heterogeneous points for many thousands of components, it can be chosen

between a component range (e.g. Components 1 – 500) and a component list. The component list is a "*.stl" file, which can be easily edited e. g. in ComponentSelection.

The maximum melting point and the maximum viscosity allow to exclude components with non-matching conditions but this criterium fails if no melting point or viscosities (Andrade parameters) are available.For all separation processes the maximum viscosity and the maximum melting point have to be declared. The knowledge of the melting point is necessary to avoid a crystallization of the entrainer. Low viscosities help to minimize the energy costs (pumping costs).

The Groups button allows to exclude components by their mod. UNIFAC (Dortmund) groups. These groups can be seen as functional groups. The

selection box allows to switch the pure component vapor pressure equation used. Possible entries are

2. Common Settings

The processes dialog contains many identical controls for four of the five processes. Only the *Absorption* page is different.
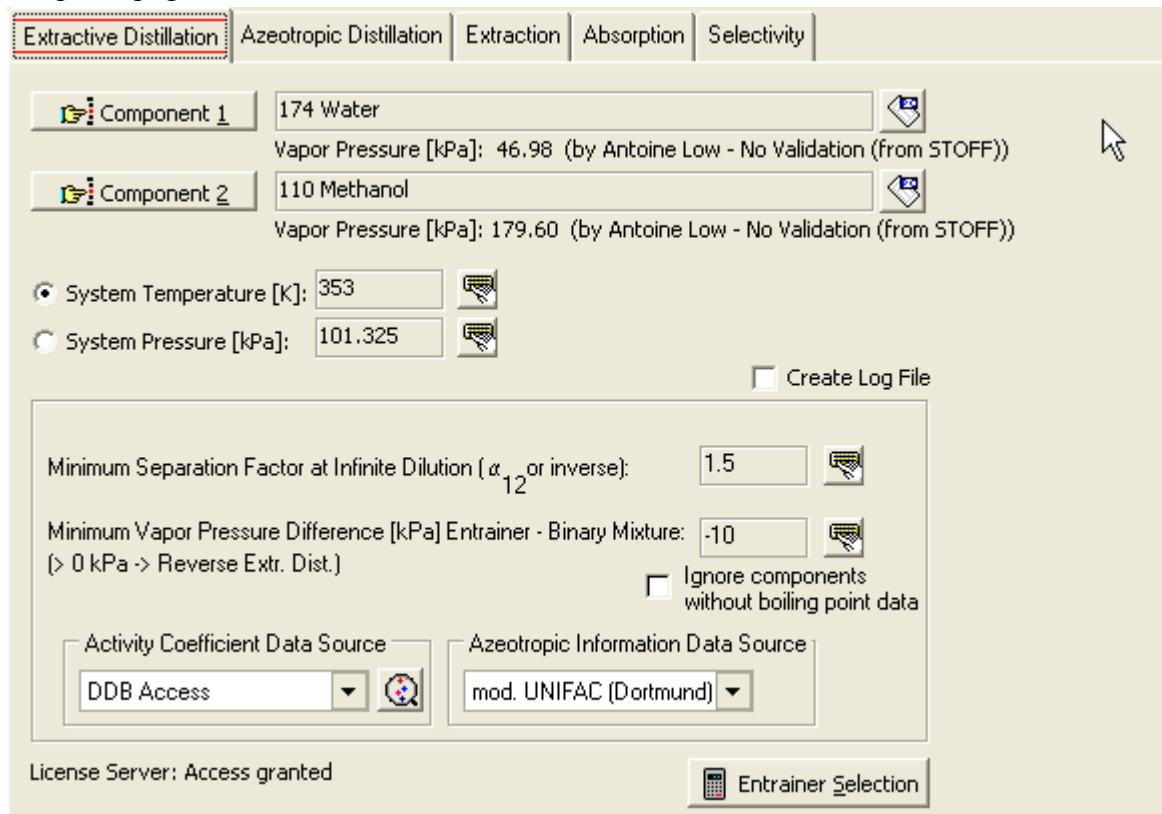
After specifying the binary separation problem (component 1 and 2), the vapor pressures or boiling points of the components are shown, depending on the chosen system temperature or pressure. The component selection ( ) is performed by the (DDB-) standard program ComponentSelection. The button allows to perform a search in the Dortmund Data Bank for pure component property of the component.
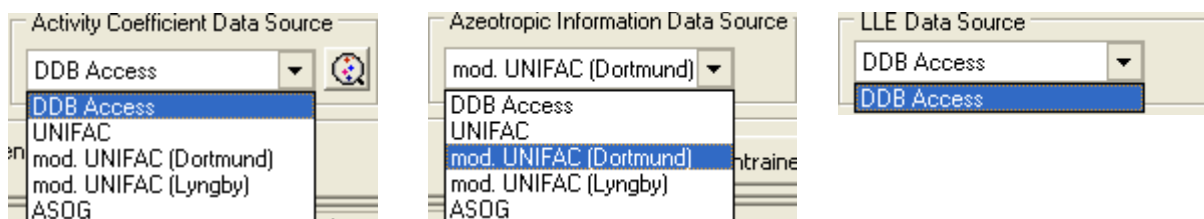
The data sources for the azeotropic data and the activity coefficients at infinite dilution have to be chosen. The LLE data are currently always taken from the Dortmund Data Bank. If experimental data are selected, a linear regression is used to estimate the values for the

separation factor or selectivity and the azeotropic temperature for the given system pressure. The calculation with four different thermodynamic models (group contribution methods) is possible: UNIFAC, mod. UNIFAC (Do), mod. UNIFAC (Ly) and ASOG.

Depending on the chosen separation process, the user has to define further input parameters:

Process	*Input*
Extractive Distillation	minimum separation factor at infinite dilution, boiling point or vapor pressure difference between entrainer and binary system
Azeotropic Distillation	selection of the new introduced azeotrope (binary or ternary), model for the calculation of the virial coefficients
Extraction	minimum selectivity at infinite dilution

If the program is finished the data finally used are stored and automatically pretended in the next run.

3. Proposal of Alternative Separation Processes

In some cases the components can be separated without introducing a third component. Therefore, a proposal with the alternative separation process is given, before the entrainer selection starts.

- zeotropic behavior $\Rightarrow$ ordinary distillation

- formation of a heterogeneous azeotrope $\Rightarrow$ heterogeneous azeotropic distillation

- zeotropy at high/low pressures $\Rightarrow$ vacuum (pressure) distillation

- strong pressure dependence of azeotropic composition $\Rightarrow$ pressure swing distillation

4. Extractive Distillation

With the help of saturation vapor pressures P_i^s and activity coefficients at infinite dilution γ_i^∞ the separation factor at infinite dilution α_{ij}^∞ for the binary system can be calculated:

$$\alpha_{12}^\infty = \frac{\gamma_1^\infty P_1^s}{\gamma_2^\infty P_2^s}$$

The entrainer should alter the activity coefficients of the components to a different extend, in order to reach separation factors far from 1. Since the entrainer should not introduce new azeotropes, the boiling point or vapor pressure difference between entrainer and binary mixture must be sufficient. For a convenient recovery of the entrainer its boiling point must usually be sufficiently higher (e.g., $\Delta T = 40$ K) than for any component of the mixture to be separated. Recent investigations have demonstrated the use of low-boiling solvents in so-called "reverse extractive distillation" processes, but as the amount of solvent has to be increased enormously to ensure a sufficient liquid concentration of the entrainer. Moreover, the enthalpy of evaporation affects the energy balance of the process negatively. Thus, this kind of process will probably only be competitive when no suitable high-boiling solvent is available.

It is also possible to switch of the boiling point / vapor pressure condition when the user puts in the value 0. This allows to find in one step entrainers both for extractive distillation and reverse extractive distillation.

If the criteria melting point, viscosity and boiling point or vapor pressure difference are fulfilled, all solvents are chosen which have a sufficient separation factor. Afterwards it will be checked, if the new solvents show a zeotropic behavior with the components to be separated.

5. Azeotropic Distillation

For the azeotropic distillation, there are two different processes available. On the one hand, entrainers are chosen which introduce at least one further extreme-boiling binary azeotrope. On the other hand, entrainers are chosen which introduce a low-boiling ternary heterogeneous azeotrope.

Tab.1   Criteria for solvents when components 1 and 2 form a pressure maximum azeotrope or no azeotrope.

Case A	Case B
• Introduction of at least one further binary azeotrope with pressure maximum • homogeneous oder heterogeneous • for a given pressure: $T_{az.1-3}$ or $T_{az.2-3} < T_{az.1-2}$ - 2.0 K • for a given temperature: $P_{az.1-3}$ or $P_{az.2-3} > P_{az.1-2}$ + 20 mmHg	• Introduction of a low-boiling ternary azeotrop • heterogeneous • for a given pressure: $T_{az.1-2-3} < T_{az.1-2}$ - 2.0 K • for a given temperature: $P_{az.1-2-3} > P_{az.1-2}$ + 20 mmHg

Tab.2 Criteria for solvents when components 1 and 2 form a pressure minimum azeotrope

Case A	Case B
• Introduction of at least one further binary azeotrope with pressure minimum • homogeneous • for a given pressure: $T_{az.1-3}$ or $T_{az.2-3} < T_{az.1-2}$ + 2.0 K • for a given temperature: $P_{az.1-3}$ or $P_{az.2-3} > P_{az.1-2}$ - 20 mmHg	there are no ternary heterogenous azeotrops with pressure minimum! Program stops.

In all cases, the method for calculating the fugacity coefficients must be specified (ideal, Tsonopoulos or Hayden and O'Connel), in order to consider the vapor phase reality.

6. Liquid-Liquid Extraction

The azeotropic data source is only required for checking the azeotropy of system $1 - 2$. In analogy to the separation factor for the extractive distillation, the extraction process demands a minimum selectivity of the entrainer at infinite dilution S_{ij}^{∞} :

$$S_{12}^{\infty} = \frac{\gamma_1^{\infty}}{\gamma_2^{\infty}}$$

For selectivities higher than 1, the solubility of component 1 in the solvent 3 is higher than the solubility of component 2 in the solvent. In this case, the binary system $1 - 3$ should have a miscibility gap. This is checked by using the LLE data bank. If LLE data are stored, the data set nearest to the system temperature is chosen, when the following options are fulfilled:

$$\left| T_{LLE} - T_{system} \right| \leq 10K \quad \text{and} \quad P_{LLE} < 50\,bar$$

It is also possible to show binary and ternary LLE-diagrams for all selected solvents. Figure 2 shows this for the system water – ethanol – benzene.
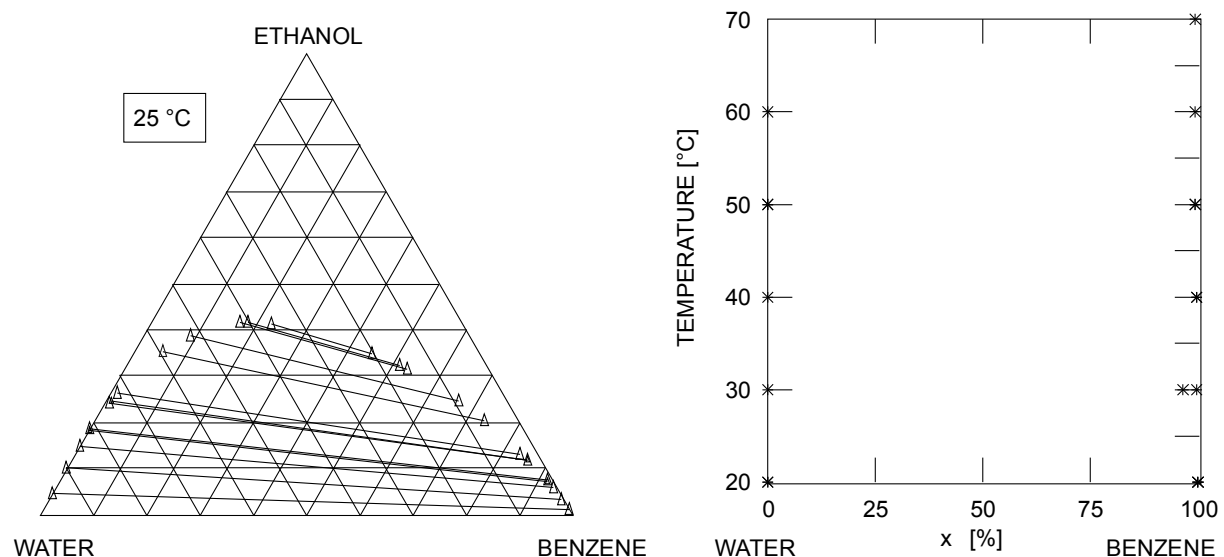

Fig.2 LLE data for the system water – ethanol – benzene

As a good method for estimating the solubility (capacity) of the components to be separated this can be done with the help of activity coefficients at infinite dilution. The KEHRWERT of the activity coefficient at infinite dilution can be taken as a measure for the capacity k_i^{∞} :

$$k_i^\infty = \frac{1}{\gamma_i^\infty}$$

The higher the capacity the more of the component to be extracted can be taken with the solvent. Since it is desirable to have both a high selectivity and a high capacity, it is possible to compare all the selected solvents in a capacity – selectivity diagram (Figure 3). In this example solvent C is the most suitable entrainer regarding capacity and selectivity.
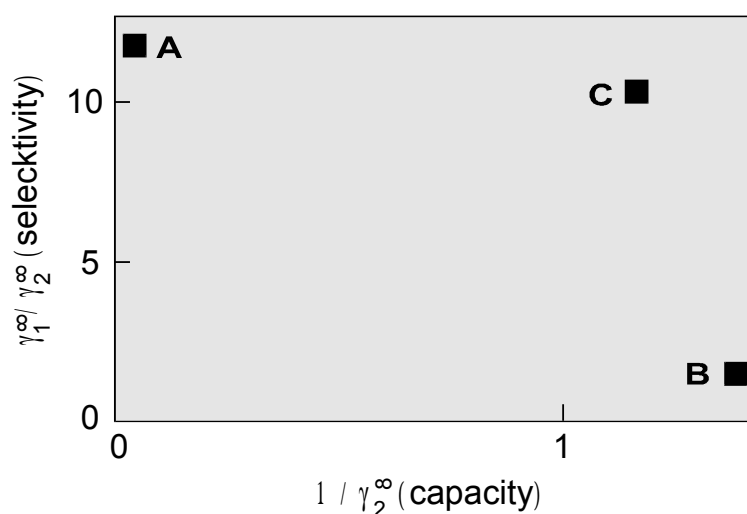

Fig. 3   Diagram capacity – selectivity for a given separation problem with the selective solvents A, B or C

Moreover, the densities of the pure components are given in the result file. If 2 liquid phases are formed, it is desirable to have a high difference in density between the 2 phases in order to have an easy phase splitting. Also the surface tensions are important factors for the design of extraction columns, since they can be used to calculate the boundary surface tension.

7. Absorption

1. Introduction

The absorption is besides the extractive and azeotropic ditisllation and liquid-liquid extraction a further important separation process widely used. The goal of the absoprtion is to separate components from a gas stream by adding an appropriate entrainer. Contrary to the extractive and azeotropic distillation process which use heat as separation entrainer the absorption and liquid-liquid extraction processes use a liquid component as entrainer.

The suitability of an entrainer depends on its ability to change the ratio of the activity coefficients of the gases to be separated. The basic condition for a good entrainer is the different solubility of the gases in the absorbent.

A further important criterium for the selection of an adsorbent is a sufficient capacity.

For estimating the selectivity of an adsorbent it is – in most cases – sufficient to know the separation factor at inifinite dilution α_{ij}^{∞}. The separation factor can be detemined by the Henry constants if $x_{Gas} \rightarrow 0$ by the relation
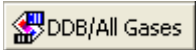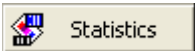
$$\alpha_{ij}^{\infty} \equiv \frac{K_{1,3}^{\infty}}{K_{2,3}^{\infty}} = \frac{H_{1,3}}{H_{2,3}}$$

Absorption exists in two types – physical and chemical. This program covers only the physical adsorption because of missing data for the chemical reaction.

2. Program Description
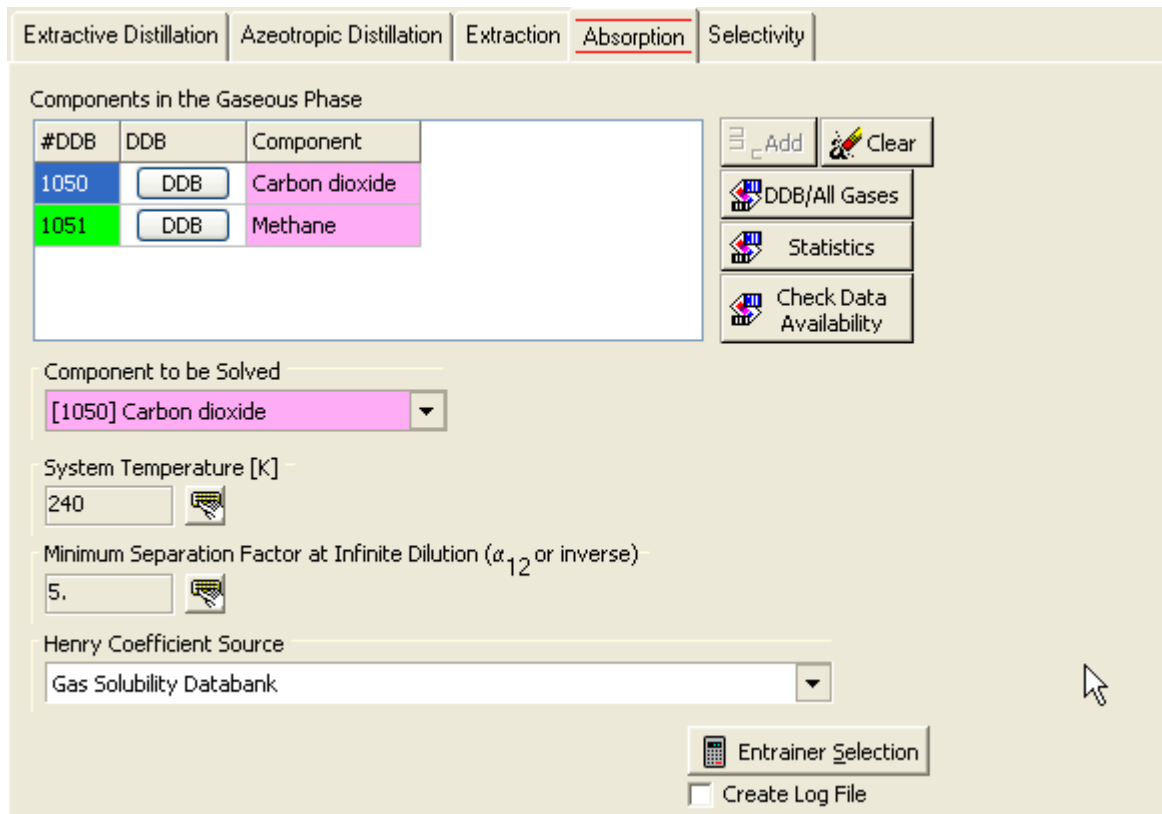
The first step is the definition of the separation problem by entering the two gases that must

be separated. The selection of the gases by the [Add] button is done with the standard DDB

program ComponentSelection. The other buttons allow to

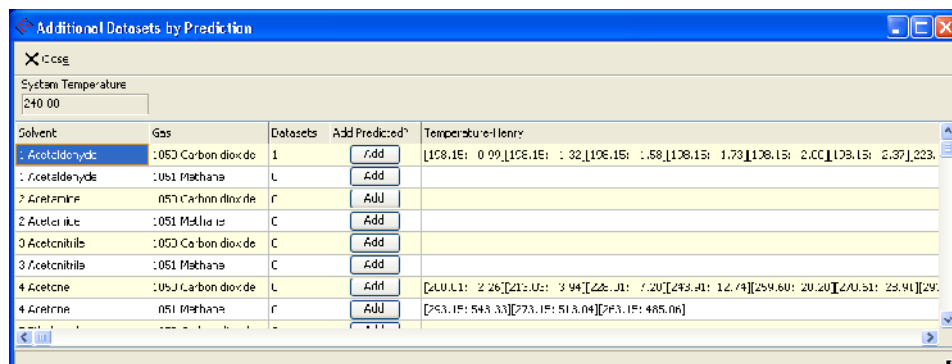| Button	Function
DDB/All Gases	... search the Dortmund Data Bank for vapor-liquid equilibrium data and gas solubilities of both gases.
Statistics	... show an overview on available data.
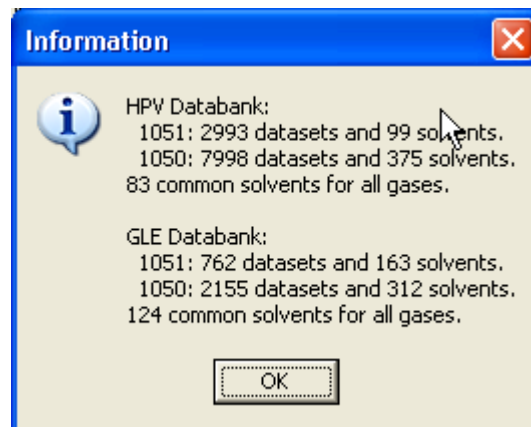
Button	Function
Check Data Availability	... search the data bank for suitable absorbents – some kind of a preview for the search.

This table shows the amount of available data for gas-absorbents pairs.

The further settings are

Setting	Description
Component to be Solved	Select the gas that should be solved better in the absorbent. This determines the sorting of the results.
System Temperature	Specify the process temperature
Minimum Separation Factor at Infinite Dilution	This value reduces the size of the result list and ignores absorbents which have a low selectivity.

The separation factors are determined by binary Henry coefficients. This program retrieves the Heny constants from

Henry Source	Description
Dortmund Data Bank – Gas Solubilities (GLE)	This data bank mainly contains experimental Henry coefficients which can be used directly. Also available Kühnen-, Ostwald-, and Bunsen-Coefficient data sets are converted.
Dortmund Data Bank – Vapor-lqiuid Equilibria Data Bank of low boiling components (HPV)	This data bank mainly contains PxT data points which have to be converted.
Predictive Soave-Redlich-Kwong model	This model is an equation of state model combined with a UNIFAC-like group contribution method.

The program also allows to read GLE and HPV data sets.

3. Data Sources

1. Gas Solubilities Data Bank

The program searches binary data sets built of one of the gases and a single solvent. This data bank retrieval normally leads to a number of Henry constants at different temperatures. To obtain the Heny constant at the selected system temperature a regression has to be performed. If at least three Henry's are available covering a temperature range of more than 10 K and if these Henry's are not farer than 50 K away from the process temperature the Henry at system temperature will be determined by linear interpolation or extrapolation. The maximum extrapolation is set to 25 K. If this regression obtained poor results (R<0.5) or if less than three points are available only direct experimental data are used. If more than a single point is available the program uses the mean value. If no exact matching points are available the program uses the nearest point if it not more than 25 K away.

The result list contains comments of the Henry determination procedure.

2. Vapor-liquid Equilibrium Data Bank

This data bank contains PxT data which have to be converted to Henry constants. The detailed procedure is a little bit to long for this program description but is covered in details in the thesis of Michael Krummen.

3. Predictive Soave-Redlich-Kwong

This data source is a model which allows to predict Henry constant from an equation of state combined with a UNIFAC-like group contribution method. This model only needs critical data and interaction parameters. This allows to calculate Henry constants for approx. 1000 components. Since this calculation is rather slow it is recommended to use the Entrainer Preselection list.

4. Result

The program collects the Henry constants for all pairs of a gas and a suitable solvent and calculates the separation factor by the equation

$$\alpha_{ij}^{\infty} = \frac{H_{1,3}}{H_{2,3}}$$

Index 1 → Gas 1, index 2 → Gas 2, index 3 → Solvent, Absorbent

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8. Entrainer Results

1. Result for Extractive Distillation, Azeotropic Distillation, Extraction, and Selectivity

1. Limited Views

The display of components can be filtered by several criteria. The *Exclude from list* criteria allow to suppress components for some information is not available.

The *Visible colums* criteria allows to suppress some spcified columns. The normal result table is often too wide even for a landscape mode print. Suppressing unused columns allows to fit the print again.

2. Sorting

This entrainer list can be arranged by different criteria:

criteria	function
selectivity	sort by selectivities
separation factor	sort by separation factors
boiling point / vapor pressure	sort by boiling points / vapor pressures
melting point	sort by melting points
surface tension	sort by surface tensions
viscosity	sort by viscosities
density	sort by densities
functional groups	sort by functional groups: about the button "functional groups" mod. UNIFAC (Do) main groups can be selected. Top: solvents which consist of the selected groups Middle: solvents which consist not only of the selected groups Bottom: solvents which cannot be incremented
component class	sort by component classes (based on mod. UNIFAC (Do) main groups): alkanes, aromatics, alcohols, water, ketones, esters, ethers, amides, halogenated compounds, unsaturated compounds, aldehydes, carbonic acids, other components
DDB code no.	sort by DDB code no.
azeotropic information	sort by azeotropic information
LLE information	sort by LLE information

3. Links

The result table contains two types of links (green underlined text): The numbers besides the component names open a context menu


```
Display Component Info
Display GLE/HPV Databank Entries
Display Pure Component Properties
```

allowing to display several further information for the solvent.

The links bnext to the selectivity columns are links to the explanation that

```
Remark <*>: Extrapolated activity coefficients for at least one component
```

2. Result for Absorption

1. Limited Views

The list of entrainers can be filtered by an allowed maximum value of Henry's constant, a maximum value of the saturated vapor pressure of the solvent, and a maximum temperature difference of the used Henry coefficients to the wanted process temperature.

2. Sorting

The sorting criteria can be all the columns from the result table:

3. Links

The result table contains two types of links (green underlined text): The numbers besides the component names open a context menu

allowing to display several further information for the solvent.

The links in the <Co> columns are links to the explanation what type of Henry coefficients have been used:

Comments
    1: Henry determined by quadratic interpolation (R>0.9)
    2: Henry determined by linear extrapolation (R>0.9)

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4: Henry determined by linear interpolation (R>0.9)
8: Henry determined by linear interpolation (R>0.5)
9: Henry determined by interpolation between two points.
```

9. Literature

M. Krummen, Dissertation, Carl-von-Ossietzky-Universität Oldenburg (2004)

D. Gruber, Dissertation, Universität Oldenburg (1999)

C. Möllmann, Dissertation, Universität Oldenburg (1996)

C. Möllmann, J. Gmehling, Auswahl selektiver Zusatzstoffe für die Rektifikation durch kombinierten Zugriff auf experimentelle und vorausberechnete Gleichgewichtsdaten, Chem.-Ing.-Tech. 69, 324 (1997)

J. Gmehling, C. Möllmann, Synthesis of Distillation Processes Using Thermodynamic Models and the Dortmund Data Bank, Ind. Eng. Chem. Research 37, 3112-3123 (1998)