Entrainer Selection

DDBSP – Dortmund Data Bank Software Package

DDB | **DDBST**
Dortmund Data Bank
Software & Separation
Technology

Contents

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, liquid-liquid equilibrium (LLE) and gas solubility (GLE) data. These data are taken from factual data banks as well as from thermodynamic models.

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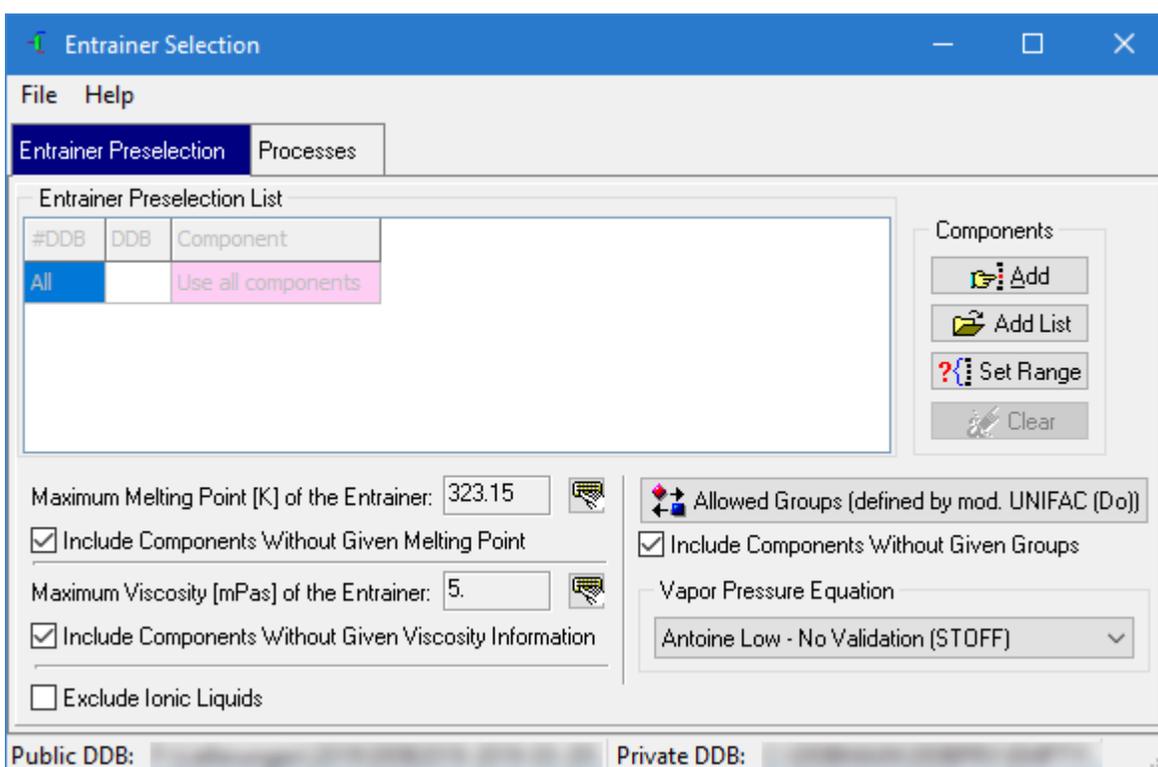
The dialog offers the possibility to specify the component range. This is useful, if the azeotropic data are calculated with a thermodynamic model. Instead of calculating the homogeneous and heterogeneous points for many thousands of components, it can be chosen between a component range (e. g. Components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

Figure 2: Vapor Pressure Equations

Figure 1: Functional Groups for Modified UNIFAC (Dortmund)

It is also possible to exclude ionic liquids completely. Ionic liquids often dominate the result lists because of their specific properties but may not be usable for the process under investigation.

2 Common Settings

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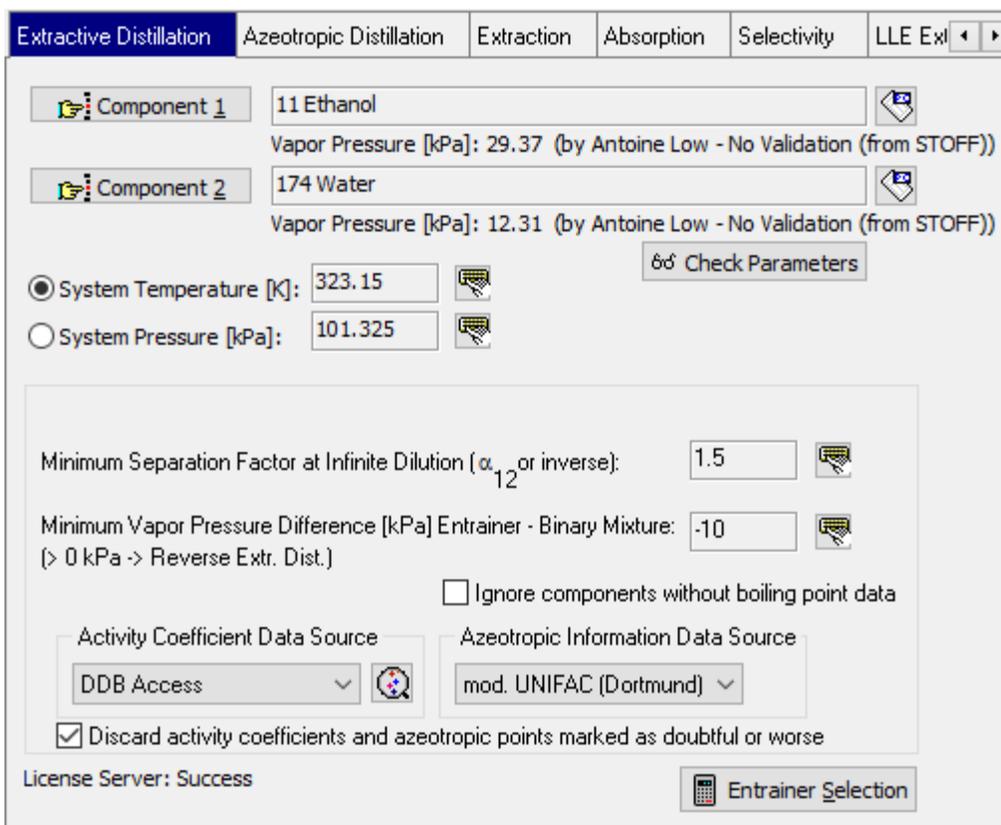
After specifying the binary separation problem (component 1 and 2), the vapor pressures or boiling points of the components are shown, depending on the chosen system temperature or pressure. The component selection (Component 1) is performed by the (DDB-) standard program ComponentSelection. The button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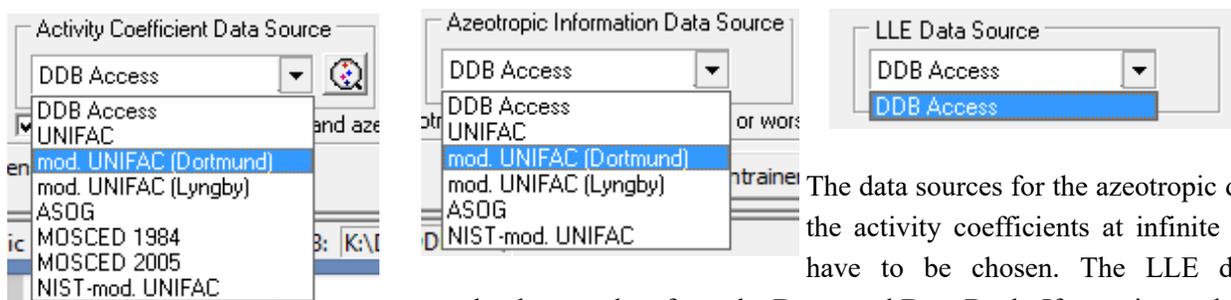
The data sources for the azeotropic data and the activity coefficients at infinite dilution have to be chosen. The LLE data are currently always taken from the Dortmund Data Bank. If experimental data are selected, a linear regression is used to estimate the values for the separation factor or selectivity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

models (group contribution methods) is possible: UNIFAC, mod. UNIFAC (Dortmund), mod. UNIFAC (Lyngby), ASOG, and NIST-modified UNIFAC (Dortmund).

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 (isobaric case) or vapor pressure difference (isothermal case) 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 entered in the next run.

3 Proposal of Alternative Separation Processes

In some cases the components can be separated without introducing a third component. The program package first checks the VLE behavior. After the evaluation 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^s and activity coefficients at infinite dilution γ^∞ the separation factor at infinite dilution α^∞ 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 off 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 show a sufficient separation factor. Additionally it will be checked, if the new solvents show 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 selected 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 azeotrope • 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 heterogeneous azeotropes with pressure minimum! Program stops.

In all cases, the method for calculating the fugacity coefficients must be specified (ideal, Tsonopoulos or Hayden and O'Connell), 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 (components to be separated). In analogy to the separation factor for the extractive distillation, the extraction process demands a minimum selectivity $S_{ij}^{\infty} = \dfrac{\gamma_i^{\infty}}{\gamma_j^{\infty}}$ of the entrainer at infinite dilution: $\quad S_{ij} \gg 1 \quad$ or $\quad S_{ij} \ll 1$

For selectivities higher than 1 ($S_{ij} \gg 1$), the solubility of component 1 in the extractive agent (component 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:

$$|T_{LLE} - T_{system}| \le 10K \qquad \text{and} \qquad P_{LLE} < 50\,bar$$

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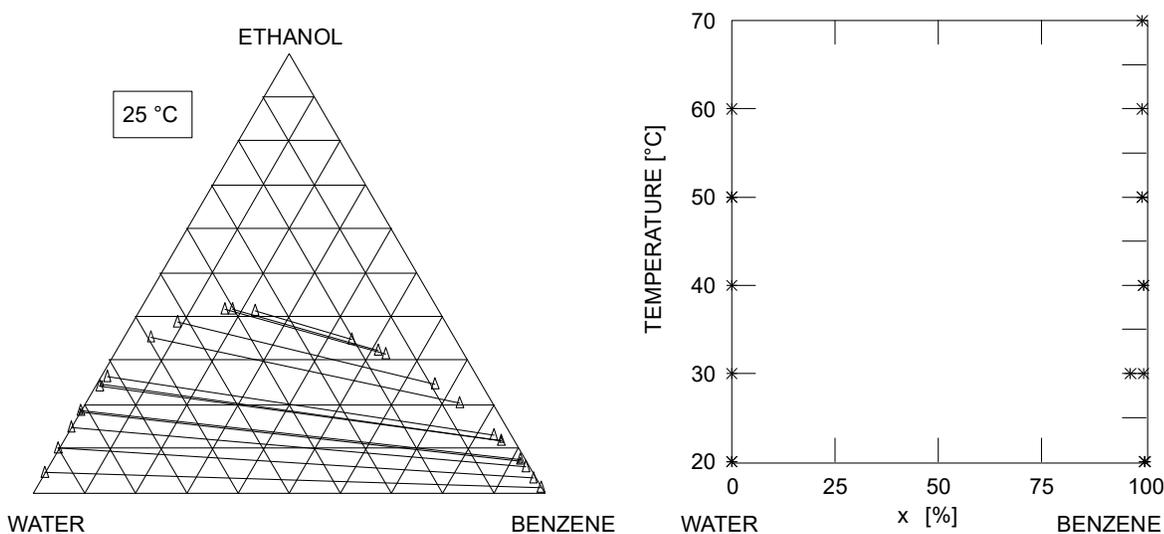
Fig.2 LLE data for the system water – ethanol – benzene

A good method for estimating the solubility (capacity) of the components to be separated is using activity coefficients at infinite dilution. The reciprocal value of the activity coefficient at infinite dilution can be taken as a measure for the capacity k :

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

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 high capacity and high selectivity.
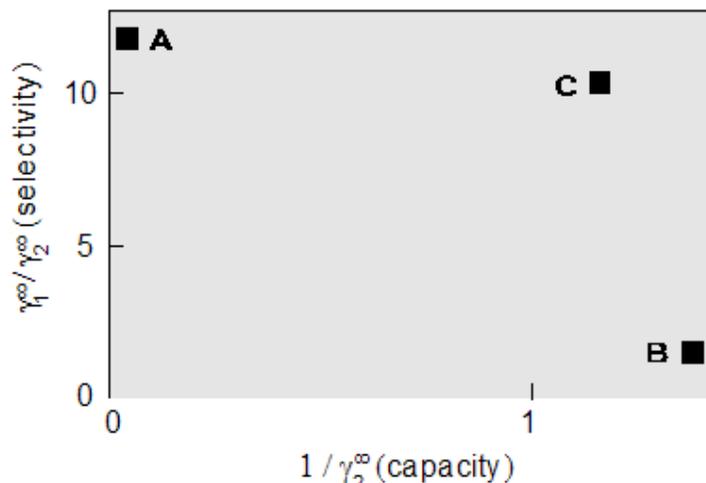

Fig. 3   Capacity – selectivity diagram for a given separation problem with the possible selective solvents A, B or C

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.

6.1 Typical Result

The binary mixture of acetone and ethyl acetate can be separated by liquid-liquid extraction with water as extractant. The selectivity of water is
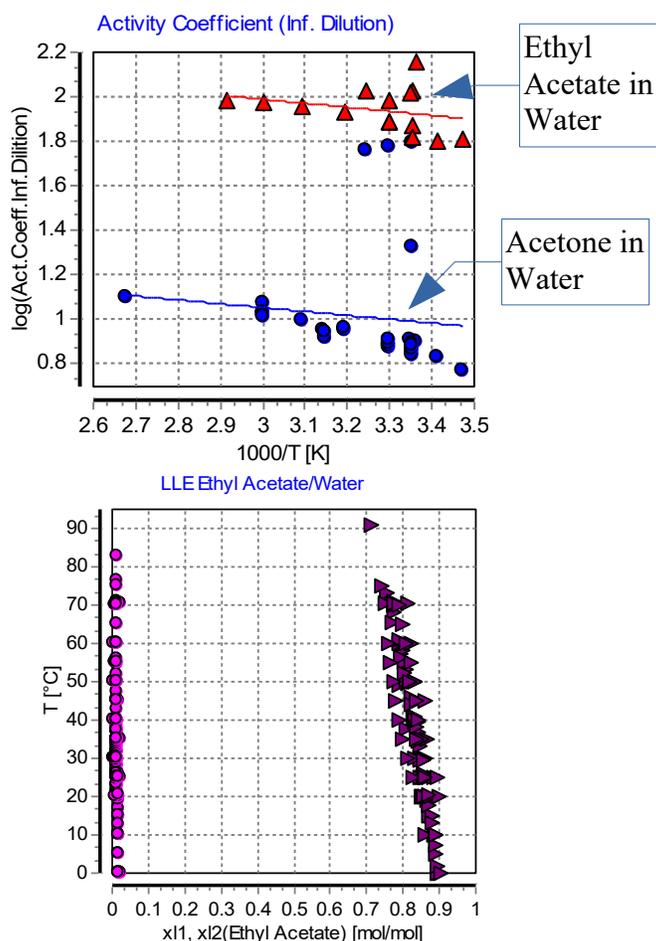
$$\frac{\gamma_{Ethyl\,acetate}^{\infty}}{\gamma_{Acetone}^{\infty}} = 10.74$$

and the capacities are

$$\frac{1}{\gamma_{Ethyl\,acetate}^{\infty}} = 0.0125257$$

$$\frac{1}{\gamma_{Acetone}^{\infty}} = 0.134626$$

Water and ethyl acetate are not completely miscible.

7 Liquid-Liquid Extraction (Extended)

7.1 Introduction

The "Liquid-Liquid Extraction (Extended)" program adds many new features to the solvent selection for liquid-liquid extraction, like, for example, the search for solvent mixtures or the use of experimental ternary and quaternary liquid-liquid-equilibria. Additionally, the density difference between the two liquid phases is calculated and the program estimates how difficult it would be to separate all components by distillation after the extraction step.

In comparison to the old program this software package does not only rely on the activity coefficient at infinite dilution for the solvent selection, but it also uses the actual distribution coefficients of the different components between the two liquid phases. The distribution coefficients show a more accurate description of the reality and can be directly used to estimate the value of the solvents for the given separation problems.

7.2 Program Description
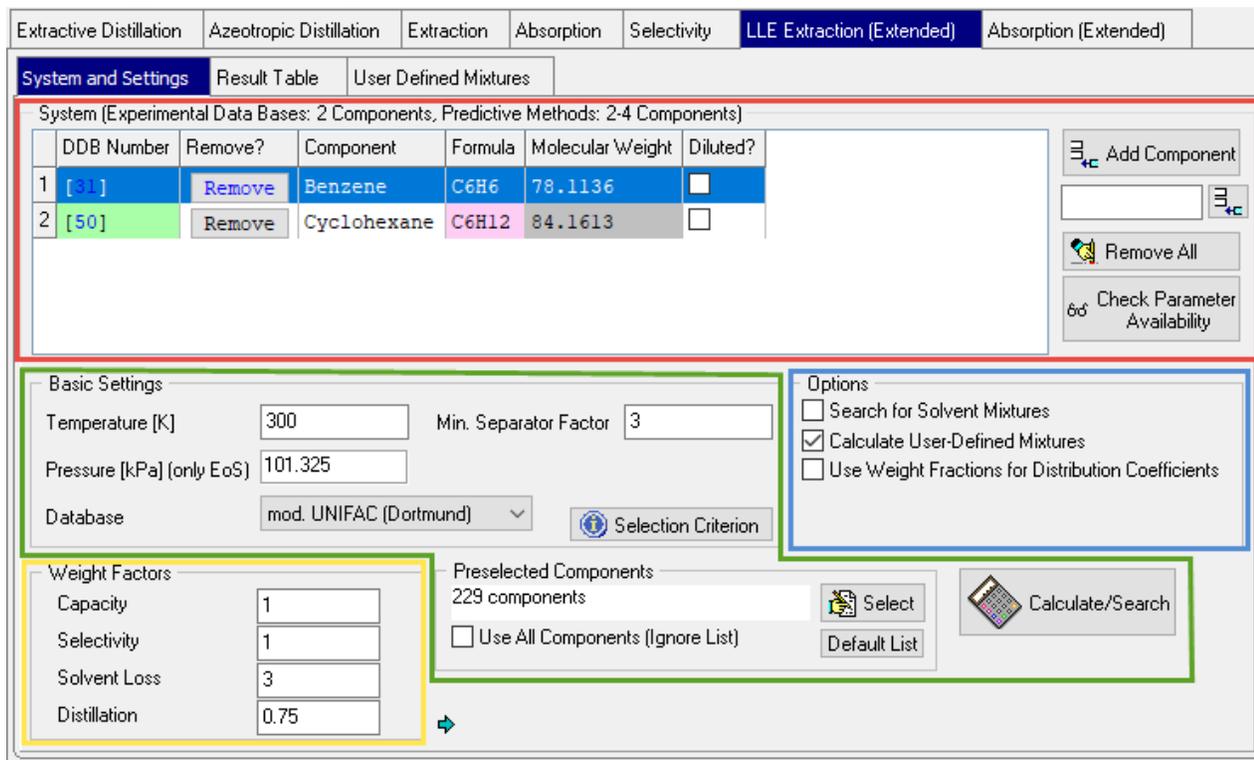
Figure 3: Main dialog of the liquid-liquid extraction (extended) program part

The dialog allows users to define the separation problem. Furthermore, the procedure and the weight of different properties for the selection of solvents can be influenced.

On the top of the dialog (red box) the components which should be separated can be defined either by the component selection (![Add Component]) or by a direct input of their DDB numbers. Two components are
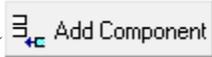
allowed if the experimental database is used. If the calculation is based on a predictive model up to 4

components are possible. The [Check Parameter Availability] button allows the user to control if all needed parameters for the chosen model for the calculation with the given components are available. The "Diluted?" check boxes can be used to mark components which are only available in small concentrations in the feed. These components are not considered to be the primary component of the raffinate phase. This option also allows marking components which should be considered for extraction. If we look for solvents which should extract component A out of a feed consisting of A and B, A can be marked as diluted.

The "Basic Settings" (green box) allows the user to define the extraction temperature and pressure (pressure only for equations of state) and a minimum limit for the separation factor of the liquid-liquid-extraction. The fitting prediction model or experimental database (LLEDDB or ACTDDB) for the solvent selection are chosen with the drop box "database".

When prediction models are used as database the considered solvents can be defined. The program starts always
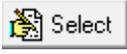
with a default list of common solvents. This list can be modified with the [Select] button, or the list can be ignored and all components of the DDB are used for the solvent selection ("Use All Components (Ignore List)").

This could lead to a time consuming calculation. The [Default List] button resets the list.

Additional settings are given in the options box (blue box) to specify the process of solvent selection. If the option "Search for Solvent Mixtures" is activated the program tries to find suitable solvent mixtures out of the combination of the suitable pure solvents. Additional mixtures can be defined in the table "User Defined Mixtures" with the help of the DDB numbers of the two solvents and the concentration of the binary mixture. They are considered if the option "Calculate User-Defined Mixtures" is marked.

The program normally uses mole fractions to calculate the distribution coefficients and the solvent loss. It is often more realistic to use weight fractions, so this possibility is given with the option "Use Weight Fractions for Distribution Coefficients".

The quality of a solvent for the given separation is directly estimated with the help of four criteria. Each of these criteria can be weighted with the given factors (yellow box) if one of the criteria should not be considered it can be set to zero. The following criteria are used:

- Capacity

    The capacity shows how easy a solvent can extract the wanted component and how much solvent is needed. For its calculation the distribution coefficients of the extracted components or, in the case of using the activity coefficient database (ACT), the inverse activity coefficient of the extracted component in the solvent are used.

$$K_i = \frac{x_{i,E}}{x_{i,R}} \qquad\qquad Sp_i = \frac{1}{\gamma_{i,S}^{\infty}}$$

- Selectivity

    A high value for the solvent selectivity shows a good separation performance for the given components with a liquid-liquid extraction. The separation factors α are used for its calculation. If the ACT database

is used, the quotient of the activity coefficients of the components, which are to be separated, in the solvent "Sa" is a measure for the selectivity.

$$\alpha_{ij}^{ext} = \frac{K_i}{K_j} \qquad\qquad Sa_{ij} = \frac{\gamma_{i,S}^{\infty}}{\gamma_{j,S}^{\infty}}$$

- Solvent Loss
  A high solvent loss to the raffinate phase leads to an inefficiency in the extraction column because this solvent has to be recycled costly. It can be estimated with the concentration of the solvent in the raffinate phase or the activity coefficient of the solvent at infinite dilution in the raffinate component.

$$solvent\, loss = \frac{1}{\gamma_{S,R}^{\infty}}$$

- Distillation
  After the extraction the solvent is normally separated from the other components by distillation. The program uses the worst separation factor which is estimated during the binary VLE calculations between the solvent and each component as the measure for the distillation efforts. It is considered as the bottleneck of this operation.

All these criteria are combined in the equation for the selection criterion

$$\left[\sum_{i=1}^{ne}\sum_{j=1}^{nr}\frac{K_{E(i)}}{K_{R(j)}}/(nc-1)\right]^{ws}\cdot\left[\sum_{i=1}^{ne}\frac{K_{E(i)}}{ne}\right]^{wc}\cdot\left(1-x_{S,R}\right)^{wsl}\cdot\log\left(\alpha_{iS}^{dis}\right)^{wsd}$$

with

nc = number of components

ne = number of components in the extract phase

nr = number of components in the raffinate phase

ws = weight selectivity

wc = weight capacity

wsl = weight solvent loss

wsd = weight distillation

$E(i)$ = component i in the extract phase

$R(j)$ = component j in the raffinate phase

$x_{S,R}$ = solvent in the raffinate phase

α_{iS}^{dis} = Worst separation factor of a connected distillation

K = distribution factor Xi,e/Xl,r

Higher values show always a better property of the examined solvent for this criterion. All criteria are summarized with the help of the selection criterion. The equation is shown when the button [Selection Criterion] is used.

The best solvent will have the highest values for this selection criterion.

The calculation is started with the [Calculate/Search] -button and can be interrupted by the [Stop] - button

7.3 The Calculation

During the calculation the program always estimates which of the given components will be the main component in the raffinate phase for the used solvent. It is the component which shows the least effort to migrate from the feed into the solvent and is not diluted. After that the binary LLE between this component and the solvent and the distribution of the other component/s at infinite dilution between these two liquid phases is calculated. This procedure is reasonable because most of the extraction steps will take place under this condition. Furthermore, the results for all solvents are comparable. Other mixture properties (like azeotropic behavior) are calculated for binary systems between the solvent and each of the given components. The solvent properties are also estimated for the pure solvent and the solvent mixture.

7.4 Results
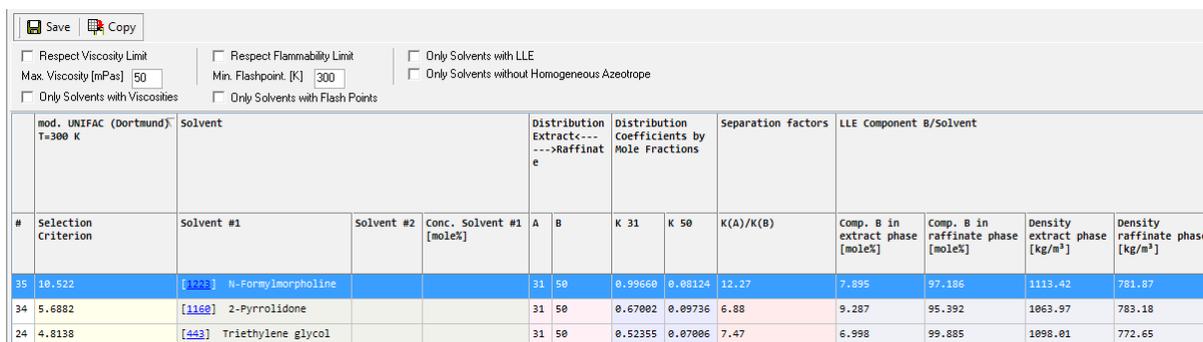
#	Selection Criterion	Solvent #1	Solvent #2	Conc. Solvent #1 [mole%]	A	B	K 31	K 50	K(A)/K(B)	Comp. B in extract phase [mole%]	Comp. B in raffinate phase [mole%]	Density extract phase [kg/m³]	Density raffinate phase [kg/m³]
35	10.522	[1223] N-Formylmorpholine			31	50	0.99660	0.08124	12.27	7.895	97.186	1113.42	781.87
34	5.6882	[1160] 2-Pyrrolidone			31	50	0.67002	0.09736	6.88	9.287	95.392	1063.97	783.18
24	4.8138	[443] Triethylene glycol			31	50	0.52355	0.07006	7.47	6.998	99.885	1098.01	772.65

Figure 4: Result table 1

AZDType 31	AZD y 31 [mole%]	AZDType 50	AZD y 50 [mole%]	alpha for x(31)->1	alpha for x(31)->0	alpha for x(50)->1	alpha for x(50)->0	Ps [kPa] Solvent	Tm [K] Solvent	Sft. [mN/m] Solvent	Vis. [mPas] Solvent	Flash Point [K] Solvent	Lower Explosion Limit [Vol%] Solvent	Upper Explosion Limit [Vol%] Solvent	Name Solvent 1	Name Solvent 2
none		none		39.99	80.50	160.55	8.27	0.0218	295.86		7.420				N-Formylmorpholine	
none		none		57.42	9928.31	99.75	855.49	1.18E-006	266.95		40.665				Tetraethylene glycol	
none		none		72.89	121.41	152.55	39.60	0.00161	299.10		12.129				2-Pyrrolidone	

Figure 5: Result table 2

The "Result table" shows the results of the different databases for the solvent selection. There are some options to adapt the result sheet to the user's needs. Solvents which have a high viscosity or a low flash point can be excluded from the list. Also solvents with no information for these two properties can be suppressed. This can also be done for solvents with a homogeneous azeotrope between the solvent and one of the components. If the

ACT database is used it can also happen that there is no information about the liquid-liquid equilibria. These solvents can also be excluded. The result list can be sorted by the values of a chosen column when a left click is done on the header of the column.

The different information areas for the solvents are classified by color in the results sheet. Single red cells show a bad property of a solvent.

- the first column contains the selection criterion. The sorting of the table is related to the values in this column.

- the short solvent names and its DDB numbers are given ("Solvent" column). In a case of a binary solvent mixture the concentration of the first named solvent in the mixture is also given.

- the column "Distribution" shows which components are more likely to be extracted (left side) by the given solvent or which components will stay mainly in the raffinate phase. The component in the last column is the main raffinate component for this solvent (see calculation description).

- in the next main column the distribution coefficients of the different components are displayed.

- the separation factors are calculated in relation to the distribution coefficient of the main component of the raffinate phase.

- the column "LLE Component / Solvent" contains the information of the binary liquid-liquid equilibria between the solvent and the main component of the raffinate phase and the densities of the two liquid phases.

- the following columns ("Azeotropic information") show the azeotropic behavior at a pressure of 1 bar between the solvent and each component. If an azeotrope was detected its concentration is also given.

- the next columns ("Alpha distillation") give the separation factor for a distillation at 1 bar between the solvent and the components in their diluted regions.

- the table is closed with the solvent properties and the complete solvent names.

When the experimental database is used, no separation factors α for the distillation are estimated. The activity coefficient database uses also other values for the selectivity and capacity.

Example: The program estimated that N-Formylmorpholine is the best solvent for the separation of Benzene and Cyclohexane (see Figure 3).The third main column shows that it extracts Benzene (DDB number is #DDB=31) out of Cyclohexane (#DDB=50). It shows with K=0.99660 a better distribution coefficient for the extracted benzene than the two other shown solvents and it has with 12.27 a higher separation factor. N-Formylmorpholine and Cyclohexane have a wide miscibility gap, too. The raffinate phase nearly completely exists of Cyclohexane (97.186 mole%) which results in a low solvent loss. The density difference (1119.42 kg/m³ ↔ 781.87 kg/m³) is very large, so that the phase separation between the two liquid phases should be fast. The corresponding distillation is also easy because there is no azeotropic behavior between the solvent and the components and the separation factors of the distillation are far away from one. The pure solvent properties show that the solvent is liquid and has a low viscosity.

8 Absorption

8.1 Introduction

Besides the extractive and azeotropic distillation process and liquid-liquid extraction absorption is a further important separation process widely used. The goal of the absorption process is to separate components from a gas stream by using an appropriate absorbent. Contrary to the extractive and azeotropic distillation process which use energy and a solvent the absorption and liquid-liquid extraction processes use only a solvent as separating agent.

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

A further important criterion for the selection of an absorbent is a sufficient capacity.

For estimating the selectivity of an absorbent it is – in most cases – sufficient to know the separation factor at infinite dilution α_{ij}^{∞}. The separation factor can be determined by the Henry coefficients if $x_{Gas} \to 0$ 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 absorption because of missing equilibrium constants for the reversible chemical reaction.

8.2 Program Description

es that must be separated. The

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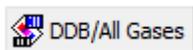
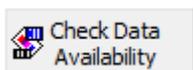| Button	Function
DDB/All Gases	... search the Dortmund Data Bank for vapor-liquid equilibrium data and gas solubilities of both gases.
Statistics	... shows an overview on available data.
Check Data Availability	Search the data bank for suitable absorbents – some kind of a preview for the search.

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

This function is only available if a component preselection (see chapter 2, Common Settings) has been made.

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 Henry constants

from

Henry Coefficient 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-liquid 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

Henry Coefficient Source	Description
	UNIFAC-like group contribution method in the g^E mixing rule.

The program also allows reading GLE and HPV data sets from file.

8.3 Data Sources

8.3.1 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 Henry constant at the selected system temperature a regression has to be performed. If at least three Henry constants are available covering a temperature range of more than 10 K and if these Henry constants are less than 50 K away from the process temperature the Henry constant at system temperature is determined by linear interpolation or extrapolation. The maximum extrapolation is set to 25 K. If poor results of the regression are obtained (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 constants determination procedure.

8.3.2 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 too long for this program description but is covered in details in the thesis of Michael Krummen[lit.4].

8.3.3 Predictive Soave-Redlich-Kwong

This data source is a model which allows to predict Henry constants from an equation of state combined with a UNIFAC-like group contribution method in the g^E mixing rule. 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 to shorten the list of potential solvents.

8.4 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

9 Absorption (Extended)

9.1 Introduction

The „Absorption (Extended)"-program adds new features to the solvent selection for absorption processes. The new program can search for solvent mixtures and can use molality-based Henry coefficients. Additionally it uses a sophisticated selection criterion for the performance evaluation of the solvents, which consists of the selectivity, the capacity and the solvent loss.

9.2 Program Description

The starting dialog allows to define the separation problem and to weight the criteria for the evaluation of the solvent performance.
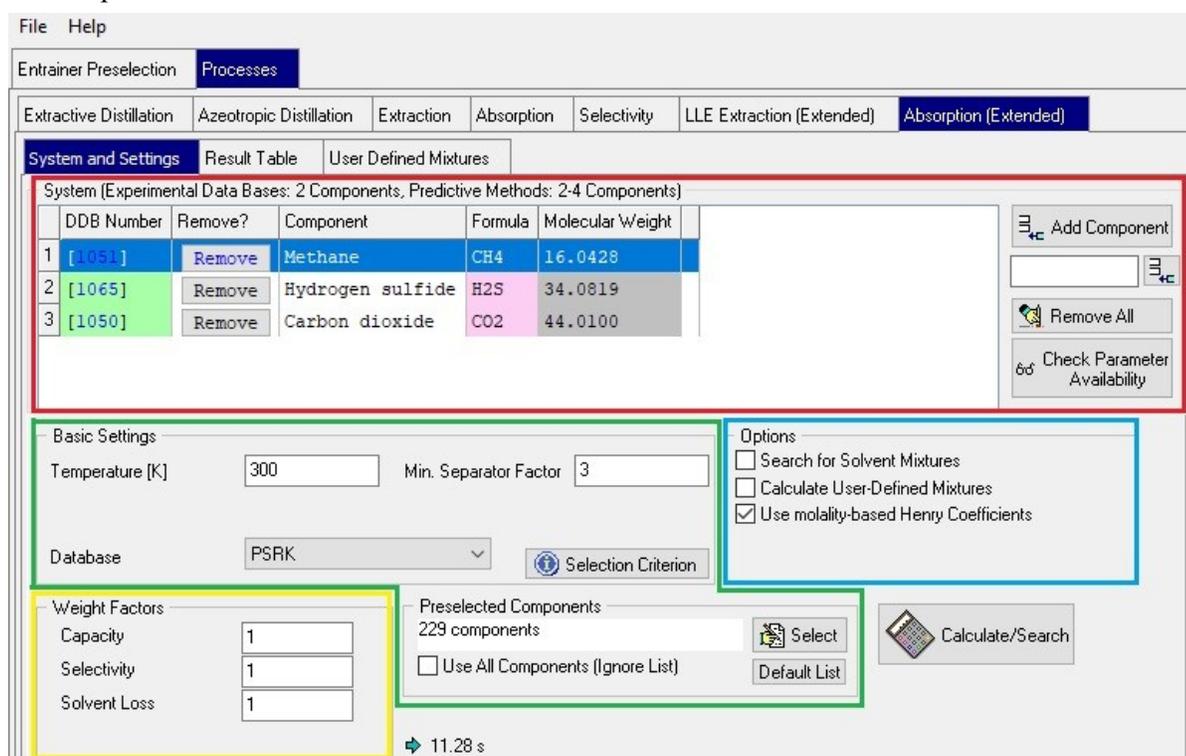
On the top of the dialog (red box) the components which should be separated can be defined either by the component selection („Add Component"-button) or by a direct input of their DDB numbers. Two components are allowed if the experimental database is used. If the calculation is based on a predictive model up to 4 components are possible. The „Check Parameter Availability"-button allows the user to control if all needed parameters for the calculation with the given components for the chosen model are available.

The „Basic Settings"(green box) allows the user to define the absorption temperature and a minimum separation factor for the absorption process. The prediction model or experimental database (GLE + HPV) for the solvent selection are chosen with the drop box „database". When prediction models are used as database the considered solvents can be defined. The program starts always with a default list of common solvents. This list can be

modified with the „Select"-button, or the list can be ignored and all components of the DDB can be used for the solvent selection ("Use All Components (Ignore List)"). This could lead to a time consuming calculation. The „Default list"-button resets the list.

Additional settings are given in the options box (blue box) to specify the process of solvent selection. If the option "Search for Solvent Mixtures" is activated the program tries to find suitable solvent mixtures out of the combination of the suitable pure solvents. Additional mixtures can be defined in the table "User Defined Mixtures" with the help of the DDB numbers of the two solvents and the concentration of the binary mixture. They are considered if the option "Calculate User-Defined Mixtures" is marked. Normally the program uses mole fraction based Henry coefficients. Often it is better to use molality-based Henry coefficients to compare solvents with a different molecular weight. This feature can be chosen with the button „Use molality-based Henry Coefficients"

The quality of a solvent is directly estimated with the help of the given three criteria which can be weighted with the given factors (yellow box):

Capacity

The capacity shows how easy the gas can be solved in the solvent. For the calculation the inverse Henry coefficient is used.

$$C_i = \frac{1}{H_{i,S}}$$

Selectivity

A high value for the solvent selectivity shows a good separation performance for the given gases with the absorption process. The selectivity is the quotient of the Henry coefficients of the given gases in the same solvent.

$$\alpha_{ij}^\infty = \frac{H_{j,S}}{H_{i,S}}$$

Solvent loss

A high solvent loss increase the amount of solvent which is needed overtime. It is linked to the vapor pressure of the used solvent.

All criteria are combined in the following equation for the selection criterion:

$$\left[\sum_{i=1}^{na}\sum_{j=1}^{ng}\frac{H_{j,S}}{H_{i,S}}/(nc-1)\right]^{ws}\cdot\left[\sum_{i=1}^{na}\frac{1}{H_{i,S}}/na\right]^{wc}\cdot\left[\frac{1}{1+\log\left(1+P_S^s\right)}\right]^{wsl}$$

nc = number of components

na = number of absorbed components

ng = number of components in the vapor phase

ws = weight selectivity

wc = weight capacity

wsl = weight solvent loss

$H_{i,S}$ = Henry coefficient of component i in the solvent phase

P_S^s = vapor pressure of the solvent

Higher values of the different terms show always better properties of the examined solvent for the given separation problem. The selection criterion summarizes all criteria to be able to estimate a global performance value to compare the different solvents. The best solvent will have the highest value for the selection criterion.

The calculation is started with the „Calculate/Search"-button.

9.3 Calculation

During the calculation the programs estimates how good the different gases can be solved in the given solvents. It sorts the different gases in order of their values of the Henry coefficient for the given solvent and estimates the selectivity between the gases. With the help of these values a list of absorbed and not absorbed gases for each solvent is estimated. This procedure makes the result between the different solvents comparable.

9.4 Results

"The Result table" shows the results of the different databases for the solvent selection. There are some options to adapt the result sheet to the user's needs. Solvents which have a high viscosity or a low flash point can be excluded from the list. Also solvents with no information for these two properties can be suppressed

☐ Respect Viscosity Limit ☐ Respect Flammability Limit
Max. Viscosity [mPas] 50 Min. Flashpoint. [K] 300
☐ Only Solvents with Viscosities ☐ Only Solvents with Flash Points

PSRK T=300 K ▽	Solvent				Distribution Gas<--- --->Absorbed			Henry Coefficients by Mole Fractions			Separation factors	
# Selection Criterion	Solvent #1	Solvent #2	Conc. Solvent #1 [mole%]	A	B	C	H 1051 [bar]	H 1065 [bar]	H 1050 [bar]	H(A)/H(B)	H(A)/H(C)	
6	4.7612	[15] Formic acid			1051	1050	1065	59682.82400	47.90760	142.06439	420.11	1245.79
16	3.514	[75] 1,4-Dioxane			1051	1050	1065	455.29934	6.31588	56.13468	8.11	72.09
7	3.1913	[18] Methoxybenzene			1051	1050	1065	541.62569	8.96970	71.75166	7.55	60.38
45	2.5743	[284] N-Methyl-2-pyrrol...			1051	1050	1065	1129.83830	6.27546	68.40287	16.52	180.04

Solvent Properties							Solvents	
Ps [kPa] Solvent	Tm [K] Solvent	Sft. [mN/m] Solvent	Vis. [mPas] Solvent	Flash Point [K] Solvent	Lower Explosion Limit [Vol%] Solvent	Upper Explosion Limit [Vol%] Solvent	Name Solvent 1	Name Solvent 2
6.208	281.45	36.813	1.552	315.15	10.0	45.5	Formic acid	
5.329	284.85	32.646	1.154	284.15	1.9	22.5	1,4-Dioxane	
0.5404	235.65	33.301	0.965	314.15	1.2		Methoxybenzene	
0.05284	249.70		1.628	359.15			N-Methyl-2-pyrrolidone	

The different information areas for the solvents are classified by color in the results sheet. Single red cells show a bad property of a solvent.

- The first column contains the selection criterion. The sorting of the table is related to the values in this column.
- The short solvent names and its DDB numbers are given ("Solvent" column). In a case of a binary solvent mixture the concentration of the first named solvent in the mixture is also given.
- The column "Distribution" shows which gases are more likely to be absorbed (right side) by the given solvent or which components will stay mainly in the gas phase. The component in the last column is the best absorbed component for this solvent.
- In the next main column the Henry coefficients of the different gases are displayed.
- The separation factors are calculated in relation to the Henry coefficient of the least absorbed gas.
- The table is closed with the solvent properties and the complete solvent names.

10 Entrainer Results

10.1 Results for Extractive Distillation, Azeotropic Distillation, Extraction, and Selectivity

10.1.1 Limited Views

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

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

10.1.2 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

10.1.3 Links

The result table contains two types of links (green underlined text): A mouse-click on the DDB component numbers besides the component names opens 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 next to the selectivity columns are links to explanations like

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

10.2 Result for Absorption

10.2.1 Limited Views

The list of entrainers can be filtered by an allowed maximum value of Henry constants, 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.

10.2.2 Sorting

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

10.2.3 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)
    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.
```

11 Literature

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