Process and Product Design Through ICAS

Product Design – Tutorial

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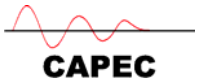
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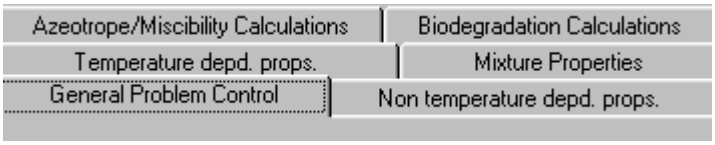
ProCamd Manual

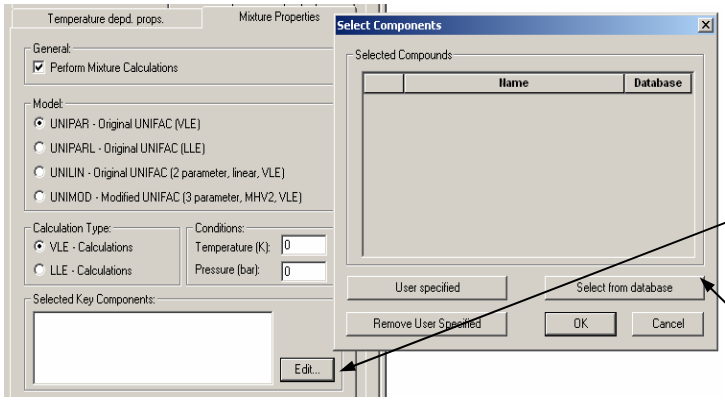
1. Introduction

To design a molecule, for example, a solvent, provide appropriate information on the following pages. In this problem, we are looking for a solvent that can replace benzene as the solvent for extraction of phenol from water by liquid-liquid extraction.



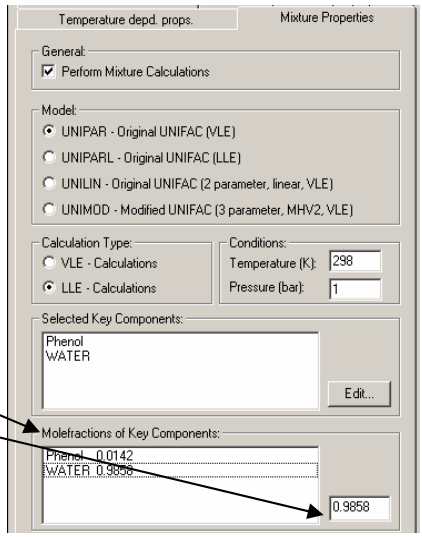
Click on  to start the calculations. In the screenshots below, the filled out pages for selection (design) of solvents for extraction of phenol from water is shown in sequential steps.

1.1. Components Selection

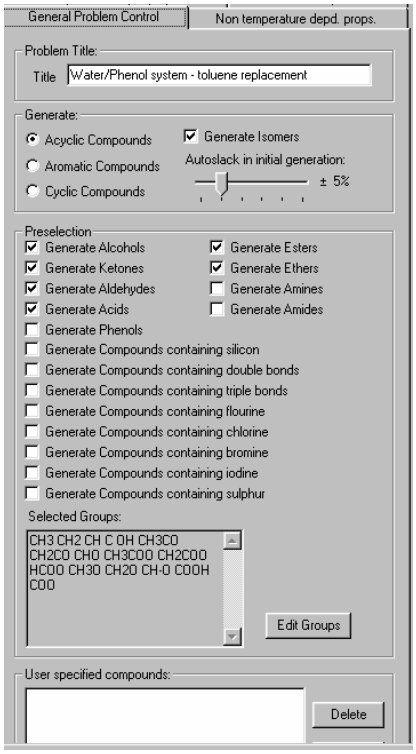


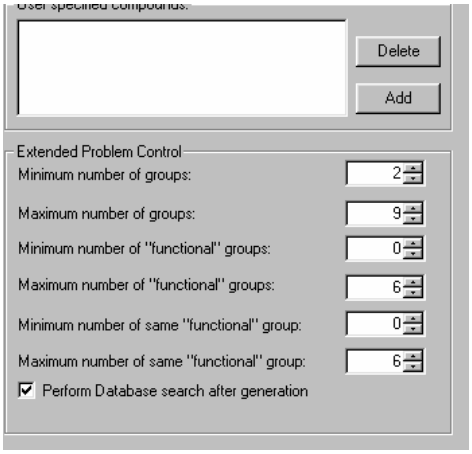
In the "Mixture Properties" tab check the "Perform Mixture Calculations" box. Click on "Edit..." in the "Selected Key Components" cage; in the displayed window click on "Select from database", the "Component Selector" window will appear: select your compounds. Click "Ok".

Enter the mole fractions. Click on the component (in the "Molefractions" cage) then type in the box the desired value and press "Enter".

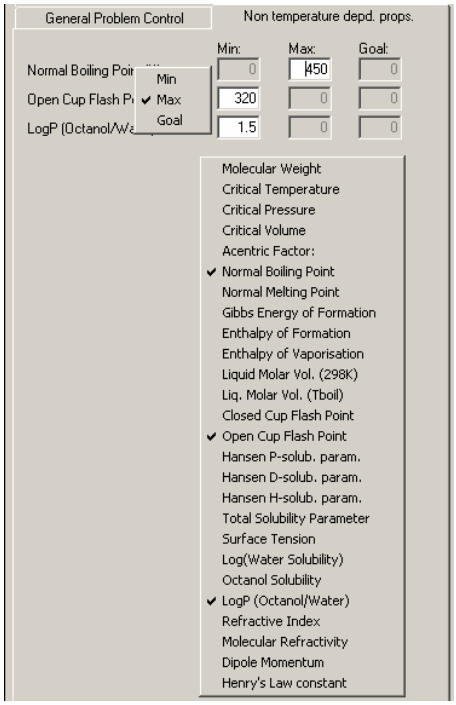


1.2. General Problem Control



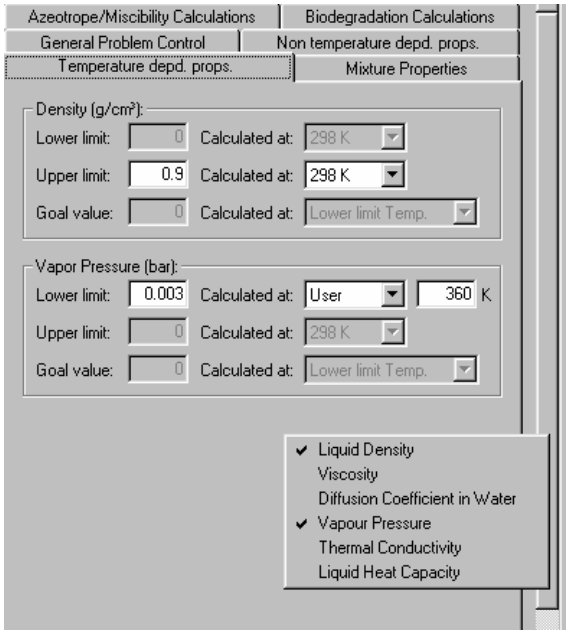


1.3. Non-Temperature Dependent Properties



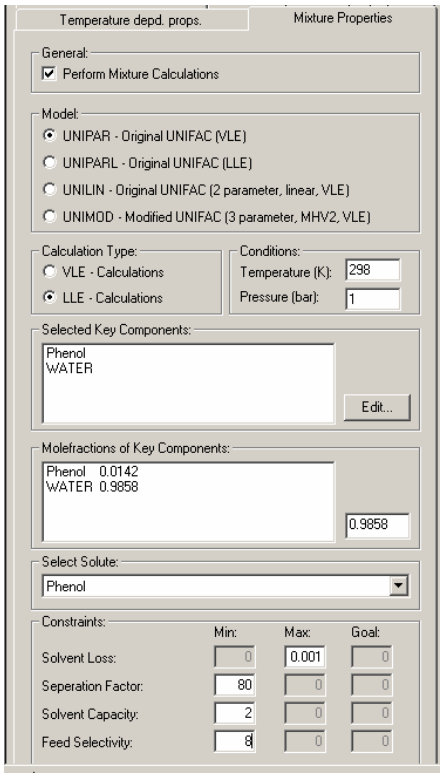
Right click on the left-hand side to obtain the list of properties. Left click on the property to select it and then fill out the data. In order to establish the limits the property can take, click on the property and uncheck the corresponding bounds.

1.4. Temperature Dependent Properties



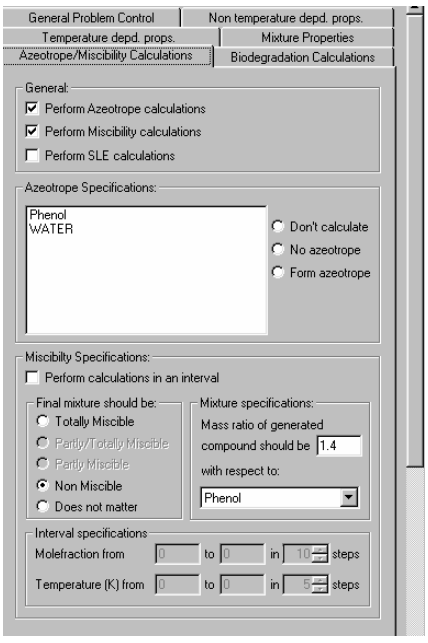
Right click on the left-hand side to obtain the list of properties. Left click on the property to select it and then fill out the data.

1.5. Mixture Properties.

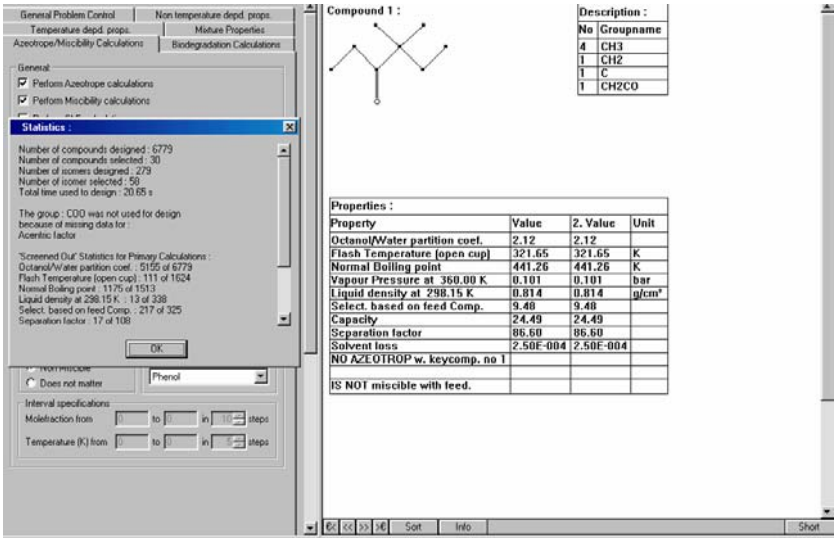


Right click on the left-hand side to obtain the list of constraints (solvent properties). Left click on "Constraints" to select it and then fill out the data.

1.6. Azeotrope/Miscibility Calculations.



- Click on  to start the calculations. On completion, the following screen is shown.



- Click OK and then use the ">>" or "<<" buttons to move up or down to see the various feasible candidate solvents. If a candidate is available in the database, "database" will be highlighted on the lower menu-bar.

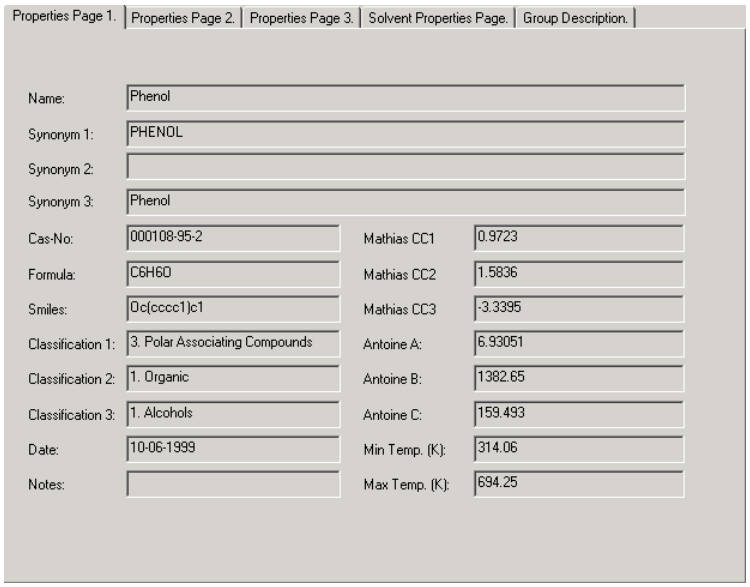
2. Exercises with ProCamd

2.1. Solvent Substitution

We have phenol deposits as a solid and we need to clean the equipment before our product can be produced. We already know that we can use benzene or toluene to dissolve the phenol. We would like to investigate if it is possible to use a more environmentally friendly anti-solvent to extract the phenol.

Step 1: Problem Formulation

We need to establish the needed properties for the replacement solvent. We can use the CAPEC database to search for the properties of phenol, benzene and toluene. In the screen shot below, the properties of phenol are highlighted (see appendix 1 on how to perform search in the CAPEC database  .



Other properties:

T_m = 314.06 K

T_b = 454.99 K

δ_{SP} = 24.63 $(MPa)^{1/2}$

H_{fus} = 11510 kJ/kmole

T_c = 694.25 K

P_c = 60.498 atm

V_c = 0.229 m^3/kmole

v = 0.889 m^3/kmole

Mw = 94.113

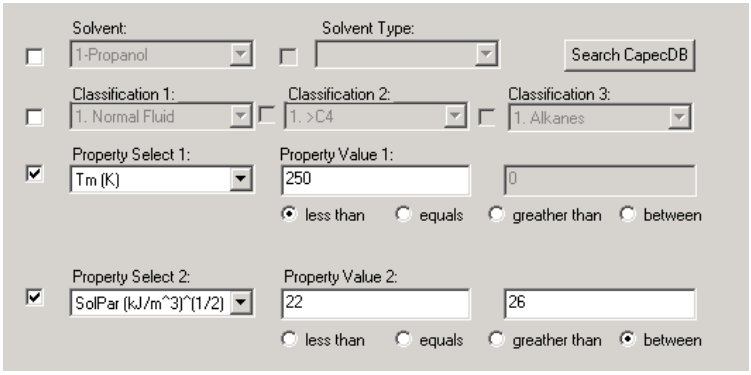
Pure component data for Phenol obtained by "basic search" in the CAPEC database

Based on the phenol data, we can formulate the solvent search problem as follows – The temperature of the operation is below 314 K (assume 300 K), at this condition, solvent

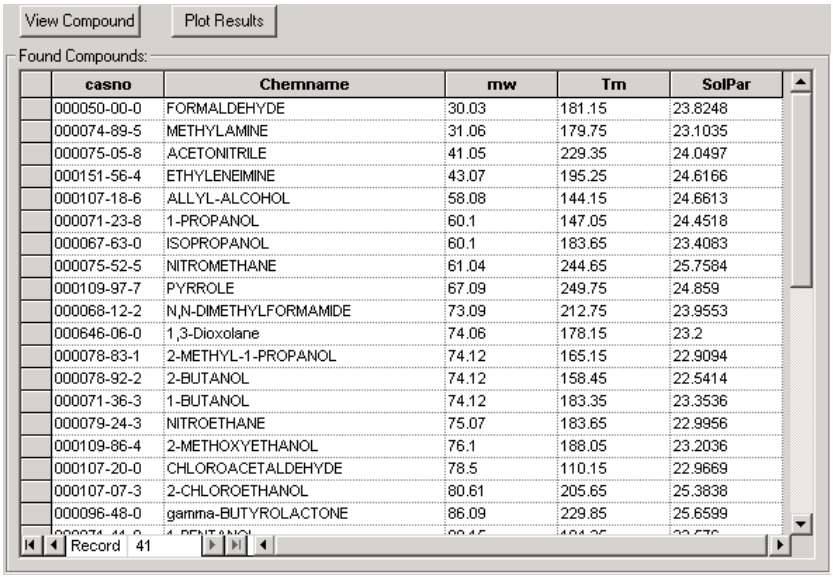
plus phenol must form a liquid solution and the composition of the phenol must be reasonably high. As a measure of solubility, initially, we can search for solvents having melting points below 250 K and having the Hildebrand solubility parameters $22 < \delta_{SP} < 26$ $(MPa)^{1/2}$. This problem can also solved through the CAPEC database (using the "advanced search" option) or ProCamd.

Step 2: Generation of candidates through CAPEC database search

To use the advanced search option in the CAPEC database, click on  and then click on "advanced search" in the CAPEC database. Then select the options for the search engine as shown below.



Now click on  to start the search engine. The search result is shown in the figure below. It can be noted that 41 candidates have been found.

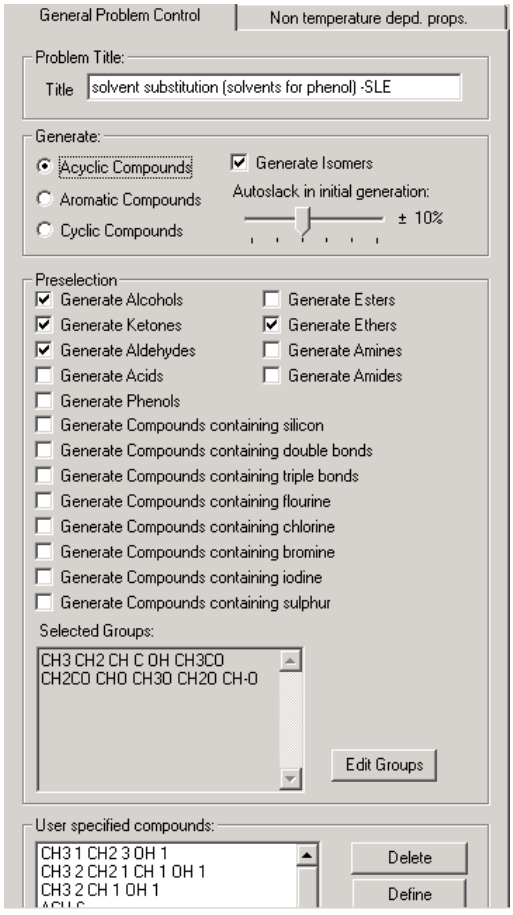


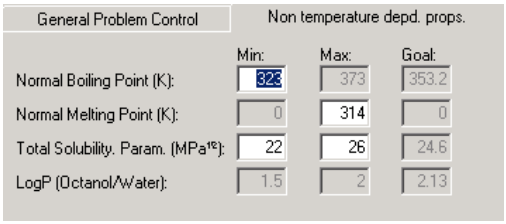
casno	Chemname	mw	Tm	SolPar
000050-00-0	FORMALDEHYDE	30.03	181.15	23.8248
000074-89-5	METHYLAMINE	31.06	179.75	23.1035
000075-05-8	ACETONITRILE	41.05	229.35	24.0497
000151-56-4	ETHYLENEIMINE	43.07	195.25	24.6166
000107-18-6	ALLYL-ALCOHOL	58.08	144.15	24.6613
000071-23-8	1-PROPANOL	60.1	147.05	24.4518
000067-63-0	ISOPROPANOL	60.1	183.65	23.4083
000075-52-5	NITROMETHANE	61.04	244.65	25.7584
000109-97-7	PYRROLE	67.09	249.75	24.859
000068-12-2	N,N-DIMETHYLFORMAMIDE	73.09	212.75	23.9553
000646-06-0	1,3-Dioxolane	74.06	178.15	23.2
000078-83-1	2-METHYL-1-PROPANOL	74.12	165.15	22.9094
000078-92-2	2-BUTANOL	74.12	158.45	22.5414
000071-36-3	1-BUTANOL	74.12	183.35	23.3536
000079-24-3	NITROETHANE	75.07	183.65	22.9956
000109-86-4	2-METHOXYETHANOL	76.1	188.05	23.2036
000107-20-0	CHLOROACETALDEHYDE	78.5	110.15	22.9669
000107-07-3	2-CHLOROETHANOL	80.61	205.65	25.3838
000096-48-0	gamma-BUTYROLACTONE	86.09	229.85	25.6599

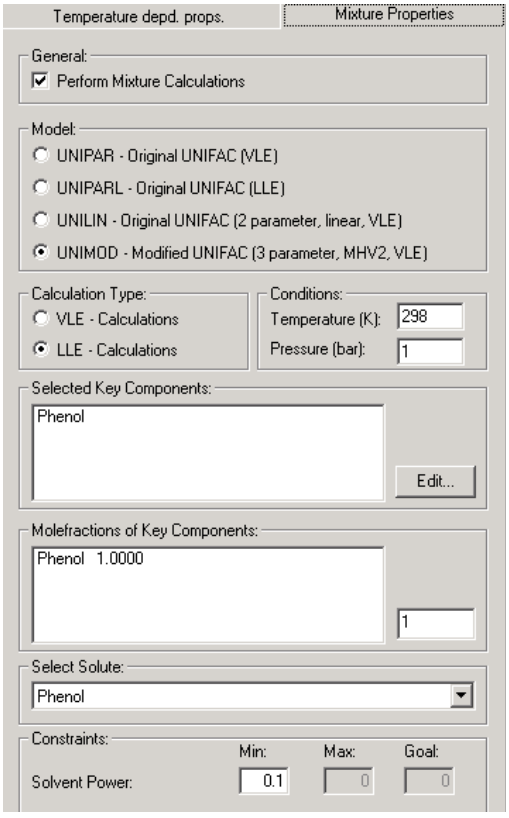
Using the results from above, the next step would be to perform a search through ProCamd, which will generate new molecules as well as check known compounds.

Step 3: Generation of candidates through ProCamd

We start by entering ProCamd from ICAS and then we need to fill-out the pages according to the instruction manual from section 1. The screens corresponding to the different pages of ProCamd are shown below.

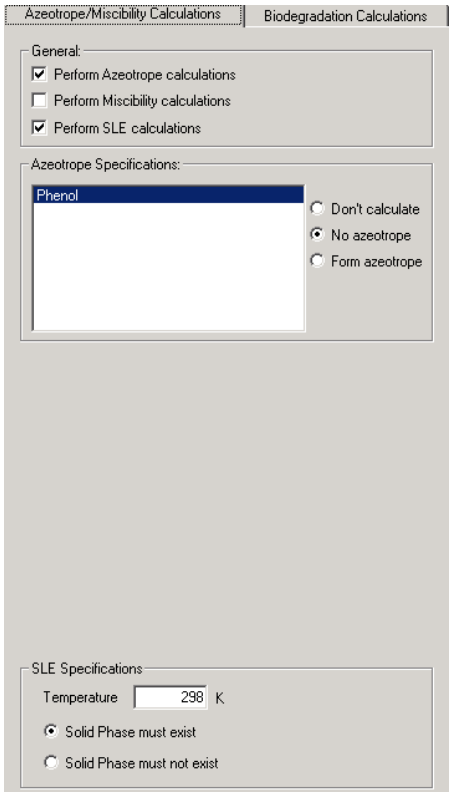




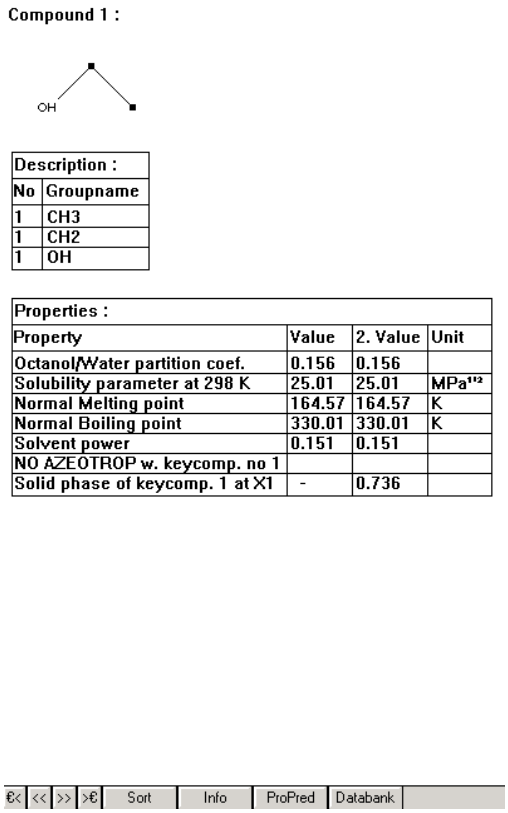


Define as user-specified compounds, some of the solvents that appear in "common solv"

Problem specification pages from ProCamd for the solvent substitution exercise

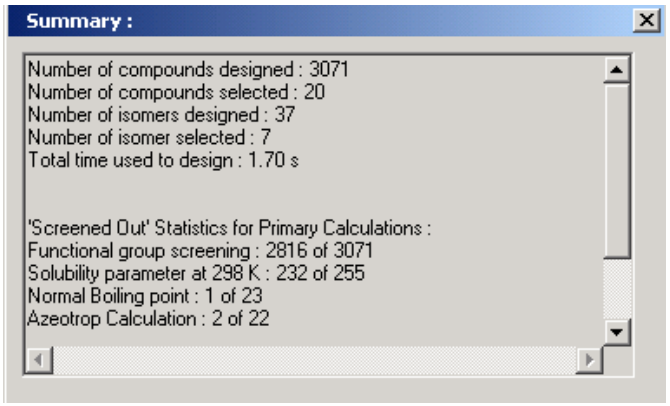


Problem specification page from ProCamd.



Results section from ProCamd. Note that "ProPred" and "Databank" are highlighted. This means that we can use these tools for this compound.

The solution statistics are shown in the figure below. This screen can also be obtained by clicking on "Info".

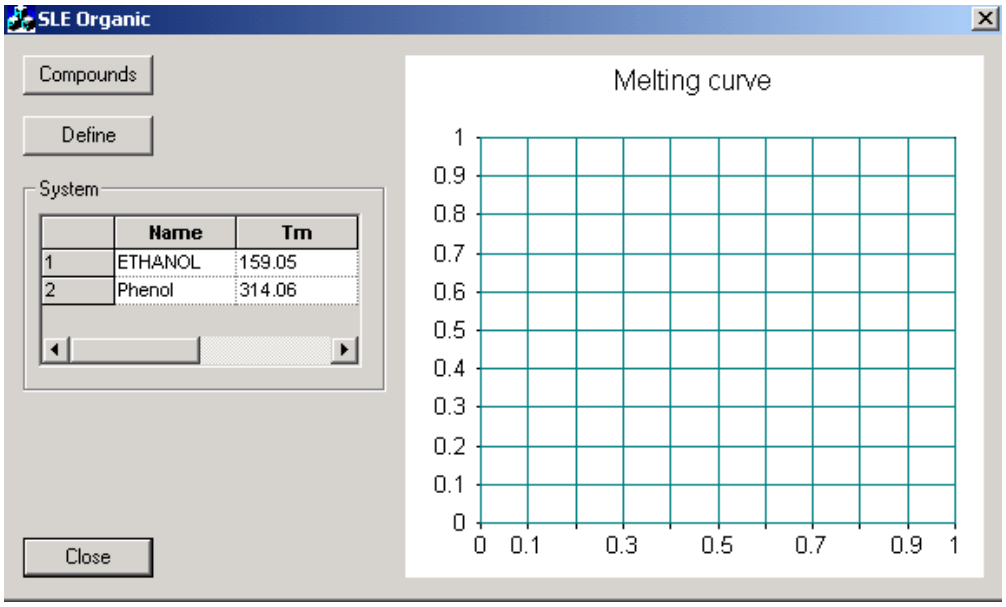


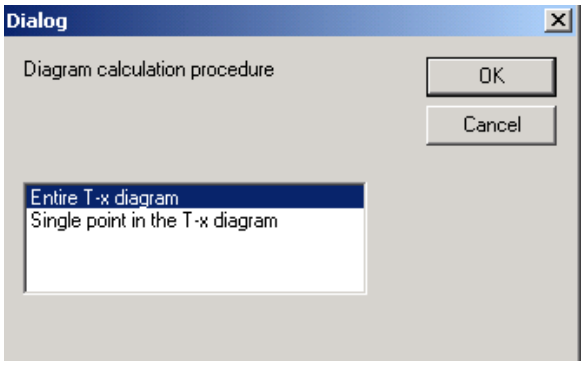
From the figures above, it can be noted that ethanol is also a feasible candidate as a solvent. We will verify the feasibility of ethanol in the next step.

Step 4: Verification of solvent through a solid-liquid equilibrium phase diagram

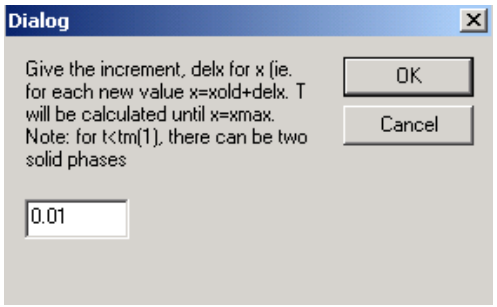
In order to obtain a solid-liquid equilibrium phase diagram, follow the steps given in appendix A3. The following steps are necessary:

1. Draw a stream in the ICAS-main window
2. Select the compounds phenol and ethanol
3. Select the property models (select UNIFAC-VLE model for liquid phase activity coefficients
4. Double click on the stream, specify the pressure (1 atm) and any values for temperature (for example, 300 K) and composition (for example, 1 and 1). Click on located on the top left hand corner.
5. Click on "Organic SLE" and then specify the data as shown below.

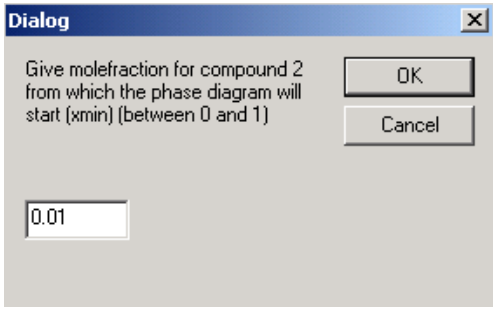




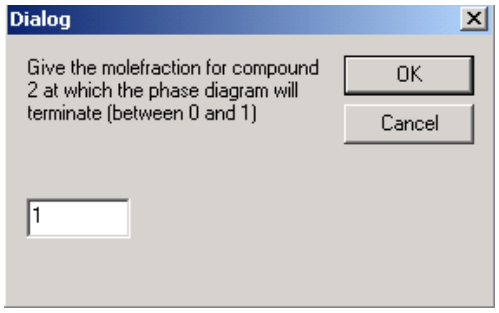
a



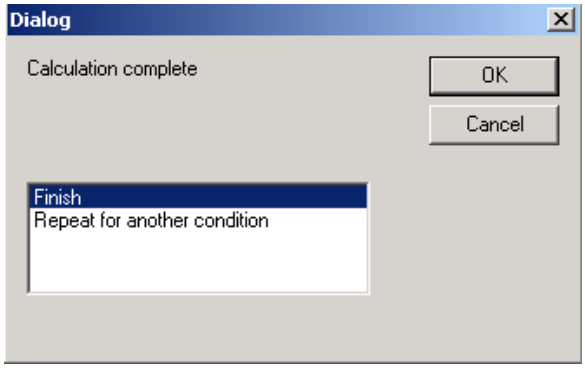
b



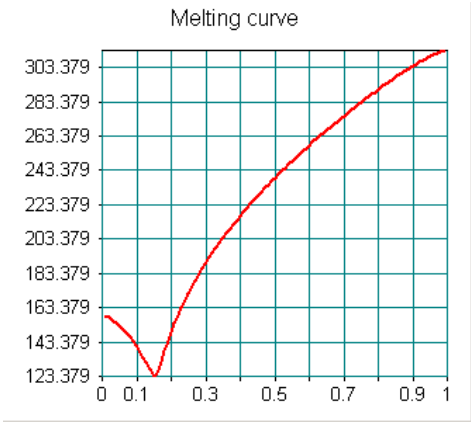
c



d



e



f

The specifications to generate the “entire T-X” diagram with the organic SLE toolbox of ICAS. Figure f shows the generated diagram. Clearly, at 300 K, a large amount of phenol can be dissolved.

Exercises related to solvent substitution

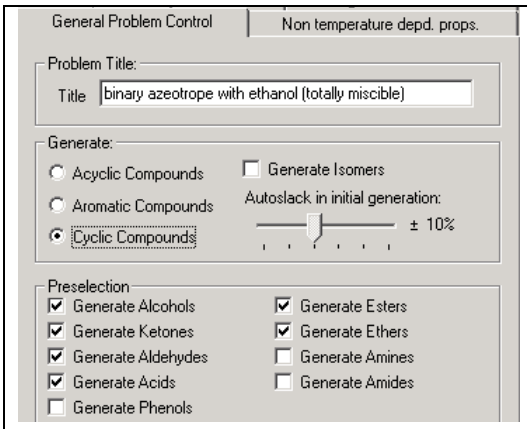
A. Solve the problem in step 2 with ProCamd (note that only the "general problem control" and the "non-temperature depd. props" need to be specified.
B. Verify another solvent through step 4
C. If you change the solubility parameter bounds to less than 22 or more than 26, will the solvents be valid for phenol? Find solute products that will be valid for solvents with solubility parameter < 22 and > 26 (use both database search and ProCamd).
D. Find solvents for Naphthalene.

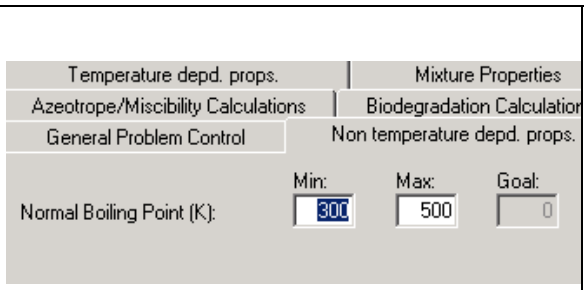
2.2. Mixture Design

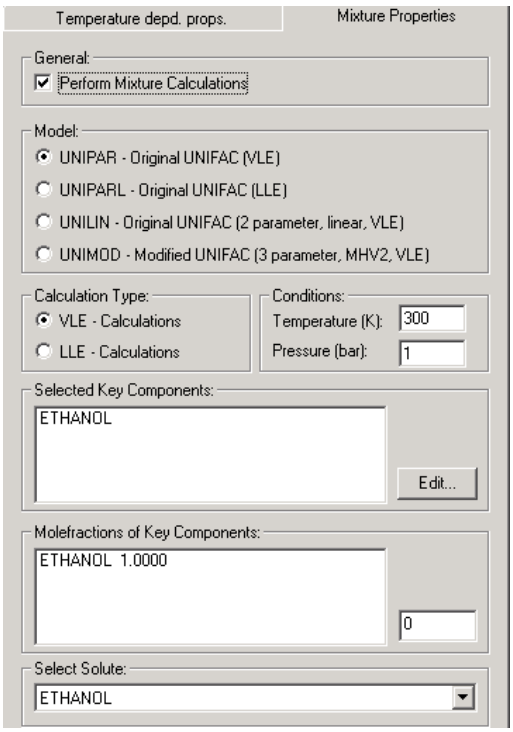
In mixture design, we specify some mixture properties that a mixture of two or more compounds needs to satisfy. Consider the following problem –

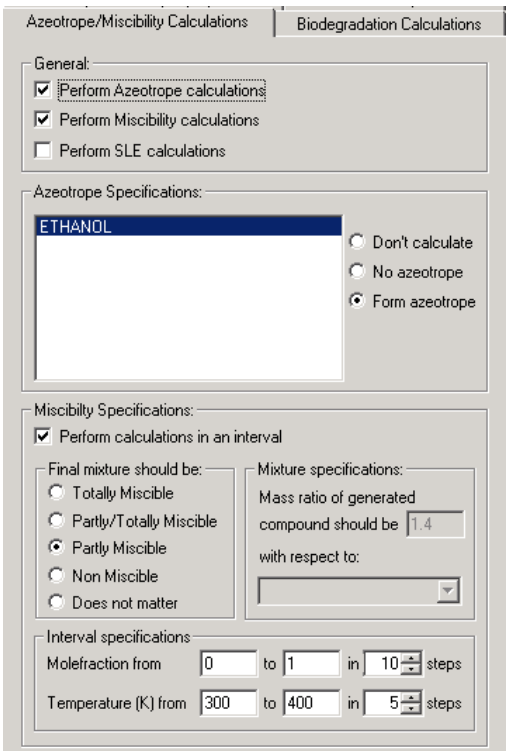
Find all binary mixtures that form an azeotrope with ethanol at 1 atm pressure and where the second compound is a cyclic compound, with 300 K < T_b < 500 K.

To solve this problem, we need to use ProCamd ("General problem control", "non-temperature depd. props", "mixture properties" and "azeotrope/miscibility" pages). A sample of the data specified is shown below.









One of the feasible mixtures is shown below (note that what ProCamd provides is the information that the two compounds will form a single-phase solution. The exact compositions will need to be calculated separately, depending on the desired mixture property, for example, the bubble point temperature.

Compound 37 :

Description :	
No	Groupname
4	CH2
1	CH2COO

Properties :		
Property	Value	Unit
Normal Boiling point	400.14	K
AZEOTROP w. keycomp. 1 at Xgen/Taz:	0.60 / 341.53 K	

Miscibility :										
T \ x	0.00	0.11	0.22	0.33	0.45	0.56	0.67	0.78	0.89	1.00
300.00	M	M	M	M	M	M	M	M	M	M
325.00	M	M	M	M	M	M	M	M	M	M
350.00	M	IM	M	M	M	M	M	M	M	M
375.00	M	M	M	M	M	M	M	M	M	M
400.00	M	M	M	M	M	M	M	M	M	M

Exercises related to mixture design

A. Repeat the above problem to find acyclic compounds that form azeotropes with ethanol
B. Repeat the above problem where the cyclic compounds do not form azeotrope with ethanol

2.3. Design of Large Molecules

Design a large molecule having the following properties,

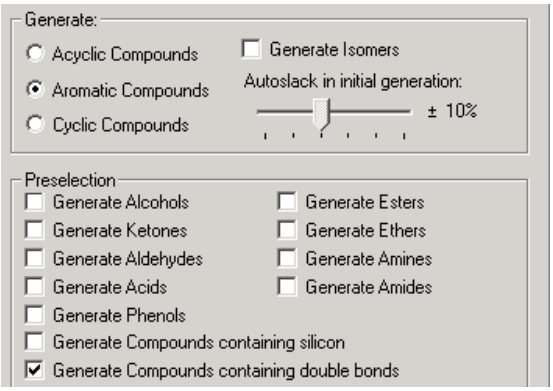
$M_w > 300$

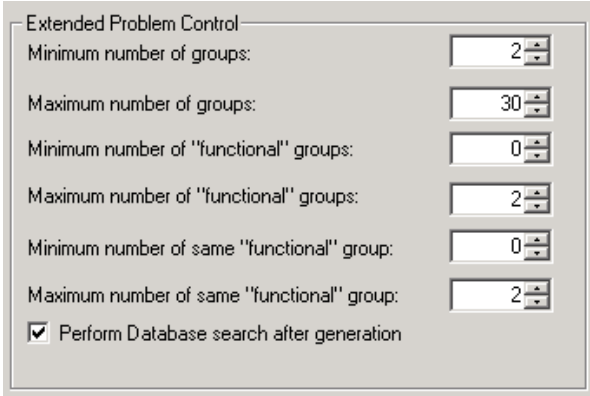
$T_b > 400$ K

$T_m > 300$ K

Solve the problem with ProCamd and then switch to ProPred and further investigate the properties of the large molecule, including further increase of the size of the molecule.

Only the “general problem control” and the “non-temperature depd props” need to be specified. In the “general problem control”, select the following,





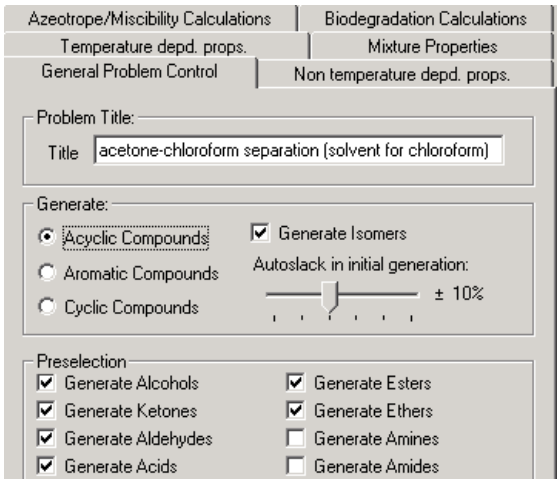
Repeat the problem for acyclic compounds and cyclic compounds

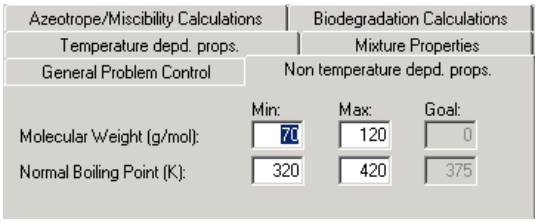
2.4. Solvent Design

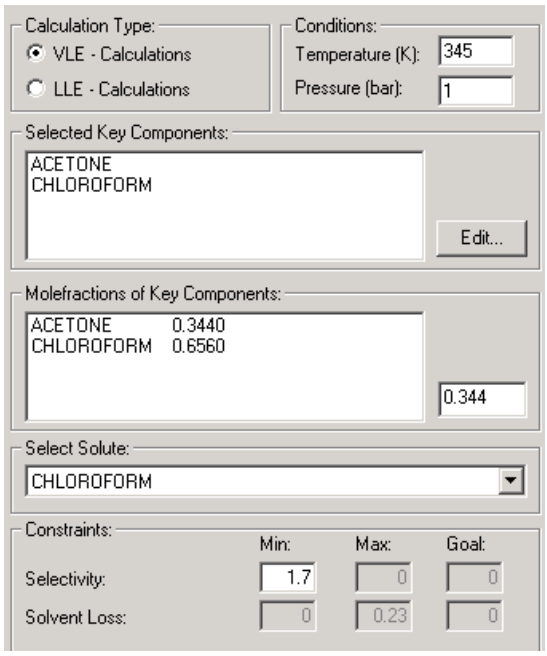
Find a solvent for the separation of acetone from chloroform. The problem definition is shown in the figures below. Use the same 4 steps as in solvent substitution problem.

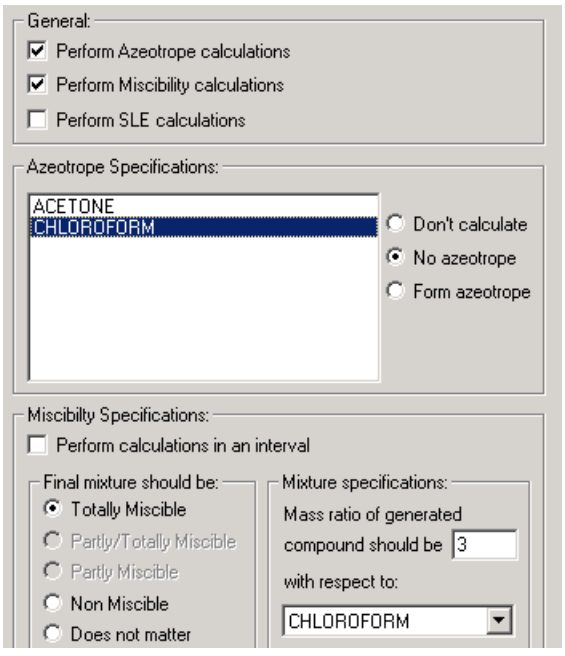
A. Define the problem with respect to pure component property targets and mixture property targets. Solvent needs to dissolve chloroform and not acetone (solubility parameter close to chloroform and not acetone. It must be liquid (boiling point higher than mixture temperature). It must be environmentally friendly (avoid aromatic compounds, chlorides, etc.)
B. Use the advanced search engine of the database to find solvents (check the properties of acetone and chloroform and then use the values of the boiling point, the melting point and the Hildebrand solubility parameter for the advanced search)
C. Use ProCamd to generate the list of feasible solvents (see figures below for the specifications)
D. Verify the solvents (in this case, perform ternary VLE phase diagrams). If solvents that are totally miscible to the feed mixture are found, then the separation will be

based on vapour-liquid systems. Tools for verification of VLE systems will be used on day 2 of the workshop.









Related problems:

Find solvents to separate acetone from methanol separation (VLE separation)

Find solvents for methyl acetate from methanol separation (VLE separation)

Find solvents for hexane-benzene separation (LLE separation)

2.5. Refrigerant Design

A refrigerant needs to have the following properties.

Use ProCamd to generate the candidates and then use ProPred to verify the selection. Generate the P-H thermodynamic diagram through ProPred to validate the refrigeration cycle.

Related problem: Design of heat pump fluid.

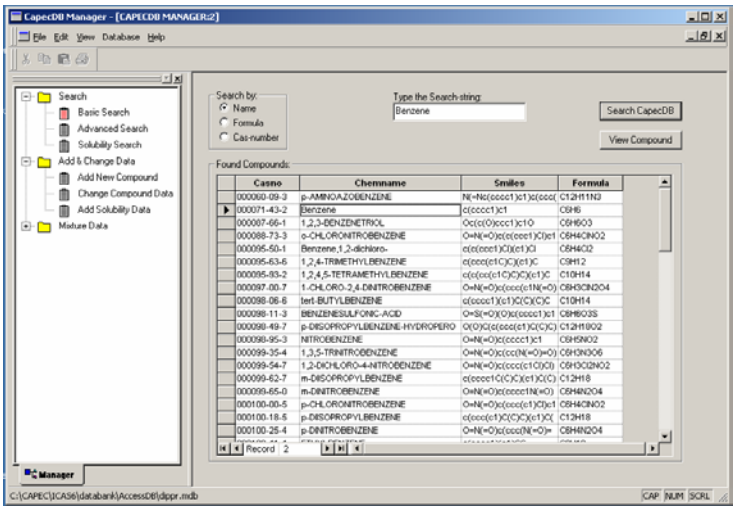
Appendix A: CAPEC Database Manager

In this section the use of the Database Manager is briefly discussed.

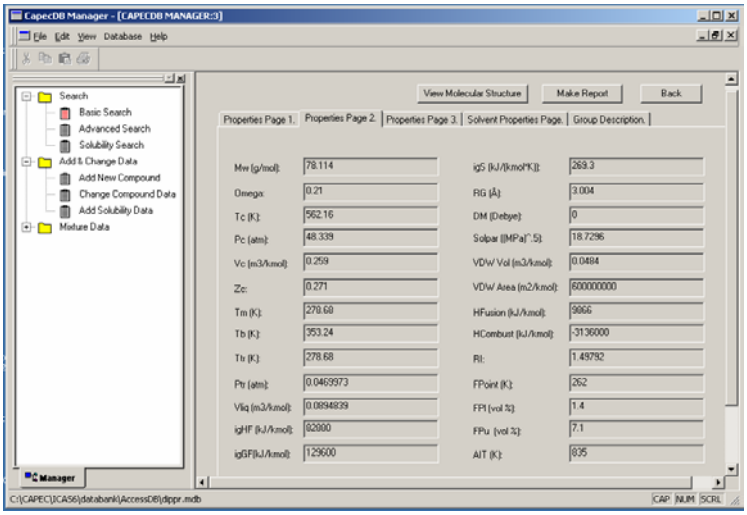
Click on the ”Database Manager” icon  in the task bar of ICAS main window.

A1. Basic Search

Under the “Search” directory in the left panel you will find different options to perform the search of a compound. Select “Basic Search” → Type the name of your component → Click on “Search CapecDB” → Select your component from the displayed list → Click on “View Compound”.

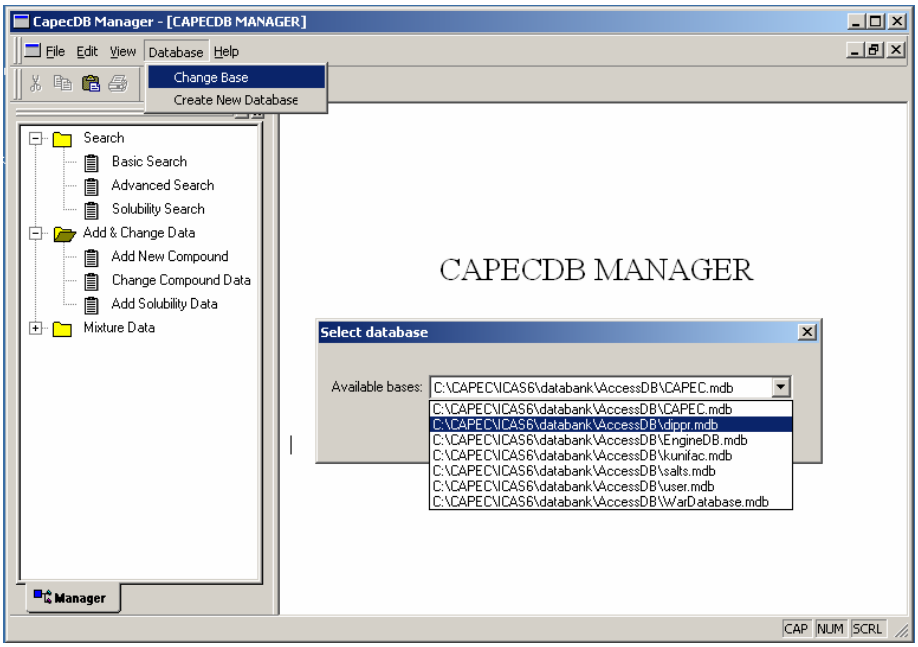


The Property pages will be displayed. Here you can find from Antoine Constants, Critical properties, property temperature dependent correlations, solvent properties and Group description. Click on ”Back” button to return to the initial page.


CapecDB Manager - [CAPECDB MANAGER:3]
File Edit View Database Help
Search
Basic Search
Advanced Search
Solubility Search
Add & Change Data
Add New Compound
Change Compound Data
Add Solubility Data
Mixture Data
Manager
View Molecular Structure
Make Report
Back
Properties Page 1.
Properties Page 2.
Properties Page 3.
Solvent Properties Page.
Group Description.
Mw (g/mol): 78.114
Omega: 0.21
Tc (K): 562.16
Pc (atm): 48.339
Vc (m3/kmol): 0.259
Zc: 0.271
Tm (K): 278.68
Tb (K): 353.24
Tr (K): 278.68
Pr (atm): 0.0469973
Vliq (m3/kmol): 0.0894839
igHF (kJ/kmol): 82900
igGF(kJ/kmol): 129600
igS (kJ/(kmol*K)): 269.3
RG (Å): 3.004
DM (Debye): 0
Solpar ((MPa)^.5): 18.7286
VDW Vol (m3/kmol): 0.0484
VDW Area (m2/kmol): 600000000
HFusion (kJ/kmol): 9866
HCombust (kJ/kmol): -3136000
RI: 1.49792
FPoint (K): 262
FPl (vol %): 1.4
FPu (vol %): 7.1
AIT (K): 835
C:\CAPEC\ICAS6\databank\AccessDB\dippr.mdb
CAP NUM SCRL

A2. Add and Change of Data

1. Data can be changed only on the user-database. Go to the user-database where your compound exists (Database → Change to any of the user-databases)

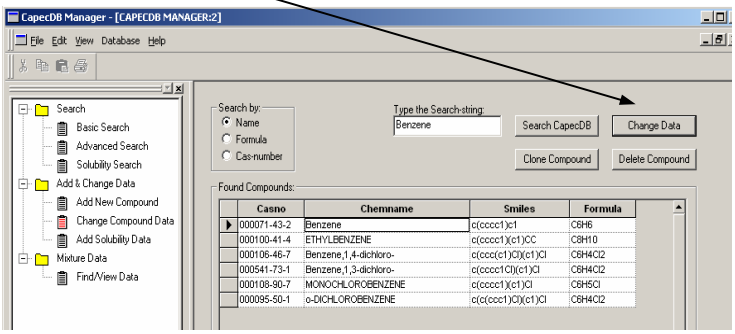


2. Change of Data:

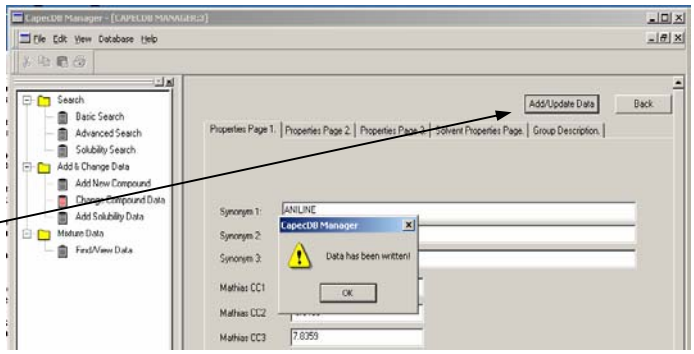
✓ Go to "Change compound data" on the left panel.

✓ Type your component in the box → click on "Search CapecDB" → Select it.

✓ Click on the "Change Data" button

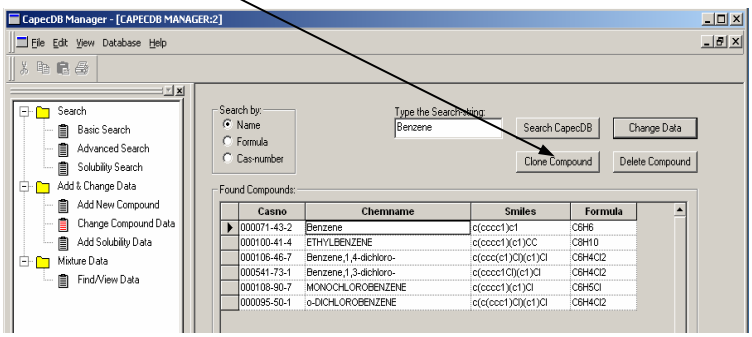


- ✓ Change the desired information in the corresponding fields. Once you finished click on "Add/Update Data" button. An updating message will appear.



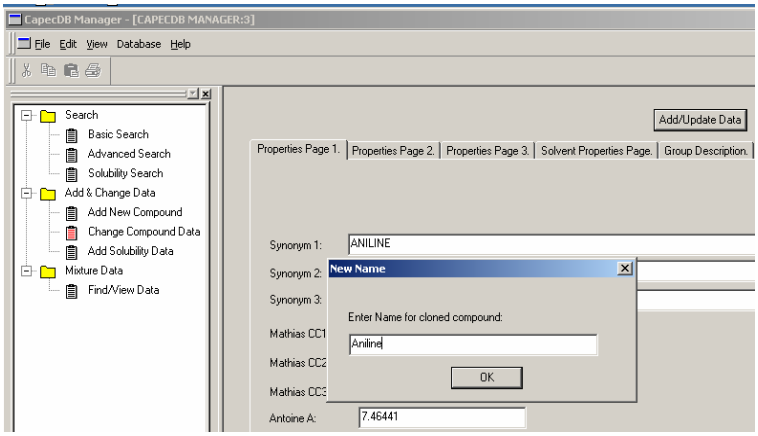
3. Clone of a Compound

- ✓ Go to "Change compound data" on the left panel.
- ✓ Type your component in the box → click on "Search CapecDB" → Select it.
- ✓ Click on "Clone Compound".

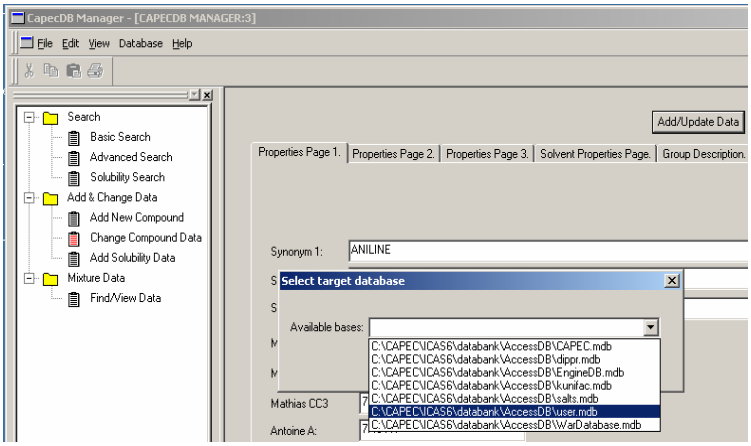


- ✓ If you change some information do it in the corresponding fields. Once you finished click on "Add/Update Data" button.

- ✓ Give a name in the "New Name" window → Click on "Ok",



- ✓ Allocate the cloned component in a database (only to the "user" database"),



- ✓ Now there is a new compound in the selected database!

A3. How to Estimate Properties of a Chemical Product Not Found in the Database?

- Launch the CAPEC database and then select the user-database.
- Click on “add/change” data
- Click on ProPred
- In ProPred, either draw the molecule or import the SMILES or import the mol.file corresponding to the chemical product. The database in ProPred can also be searched, if necessary.
- Check if all the necessary properties have been estimated by ProPred, if yes, exit from ProPred.
- Click on “update” data

Try the following exercise:

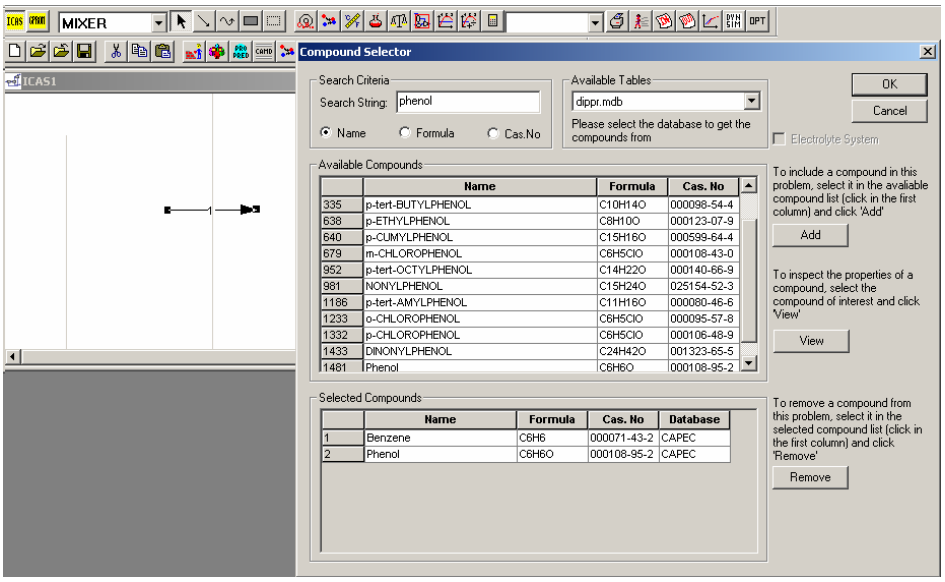
Try to put Morphine (Oc1ccc2CC3N(C)CCC45C3C=CC(O)C4Oc1c25) into the user-database. CAS number of morphine is 000057-27-2 (the database in ProPred has this compound).

APPENDIX B. Manual for SLE

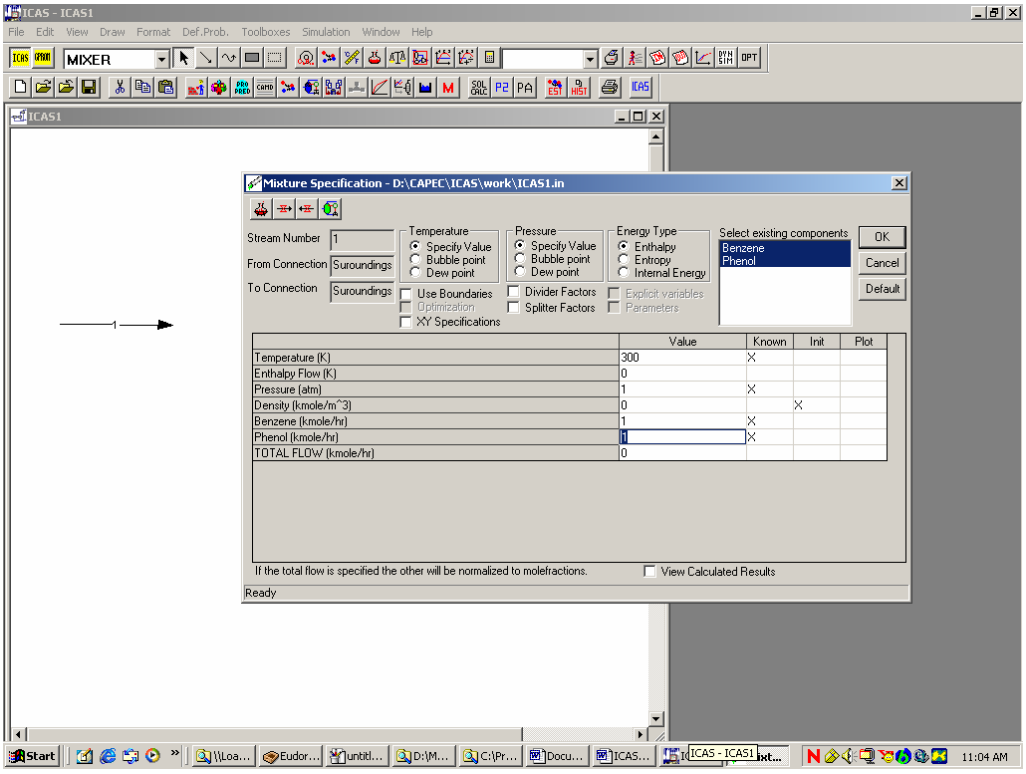
B1. Use of Utility Toolbox

B1.1. Compound selection & property model selection

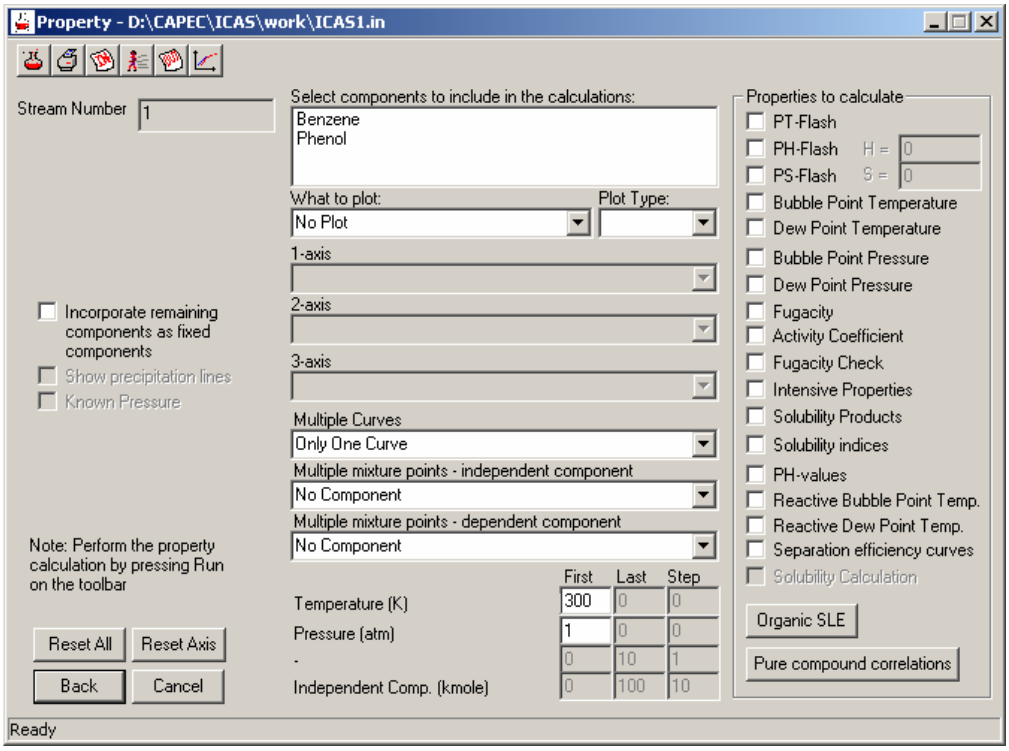
I. Draw a stream and then select compounds by clicking on the "compounds" button.



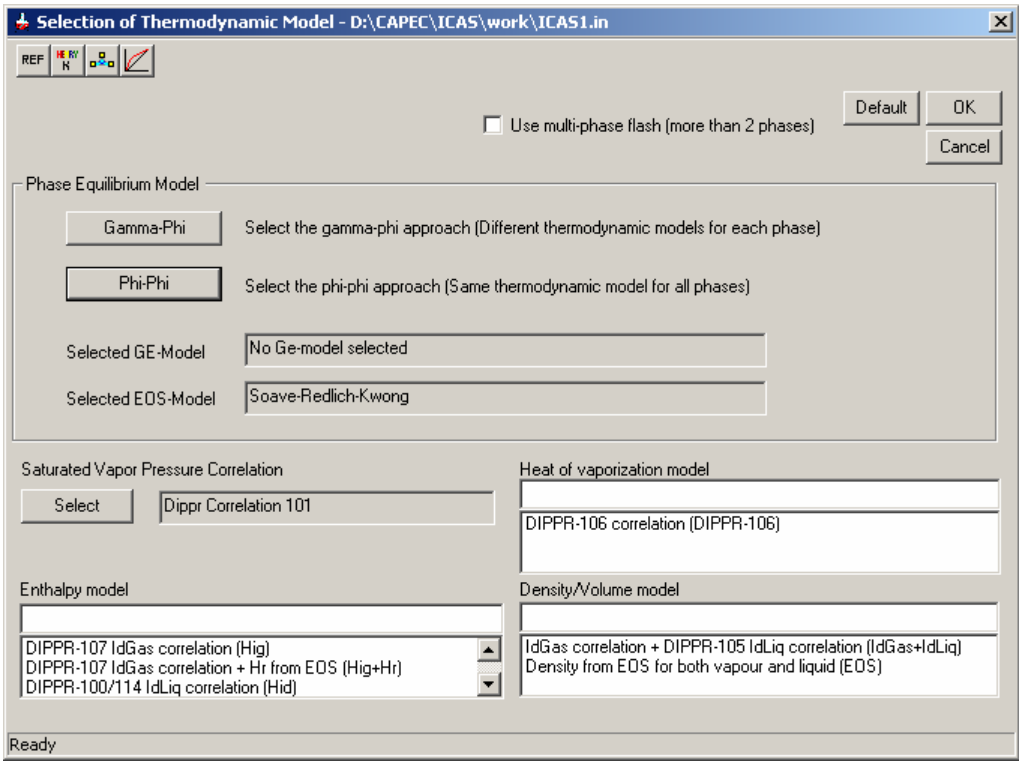
II. Double click on the stream to enter the "mixture specification" window



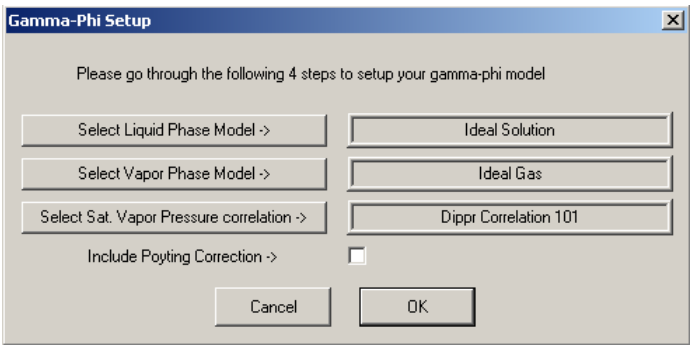
III. After specifying the temperature, pressure and component flows (as shown above) click on the top-left button  to enter the "property" window. Click on the top-left button  to go to the "property model" selection window.



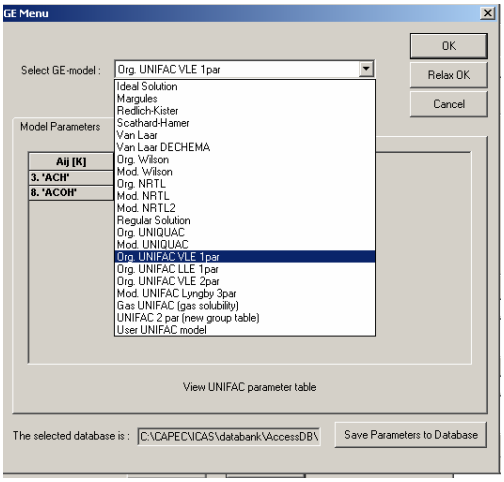
IV. Click on the “gamma-phi” option for this example

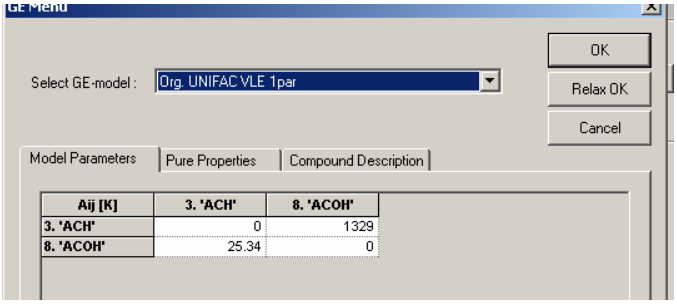


V. Click on the “select liquid phase model”

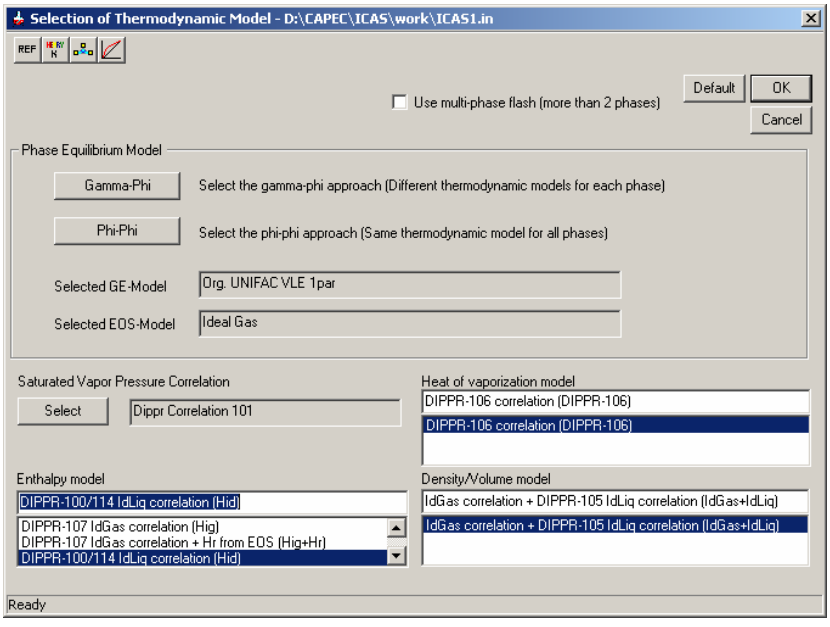


VI. Select the UNIFAC model as shown below. The UNIFAC model parameters are shown and if all parameters are available (as in this example), click OK



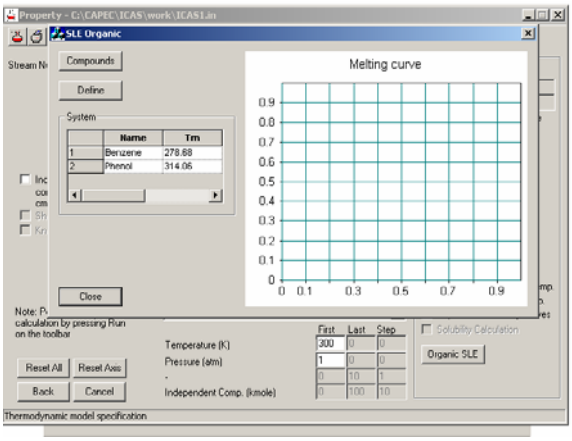


VII. On return to the main property model selection window click on default to select all the other model options (as shown below) and click OK.

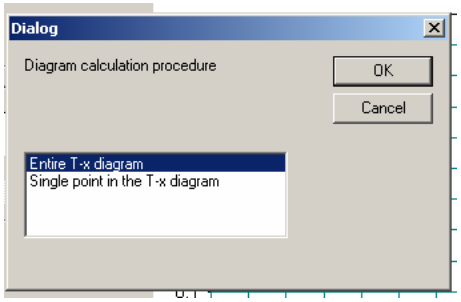


B1.2 Utility calculation option (SLE)

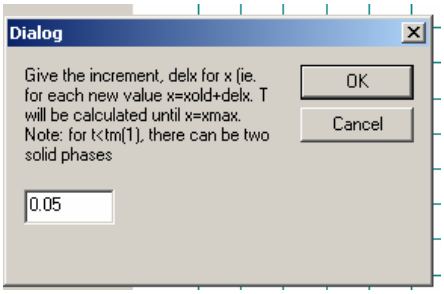
I. On return to the Property "Utility" window, select the option(s) of choice for calculations. For this example, select the "SLE" option and follow the screens SLE-a to SLE-f.



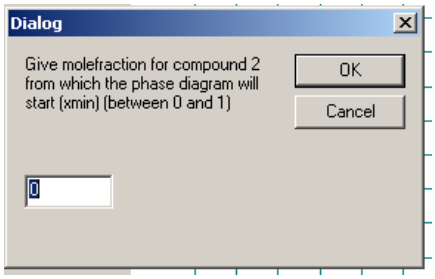
SLE-a



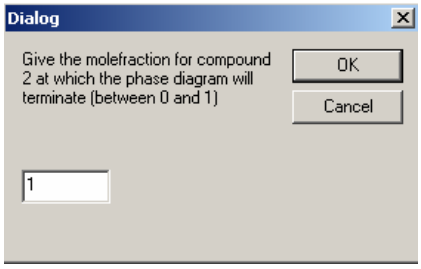
SLE-b



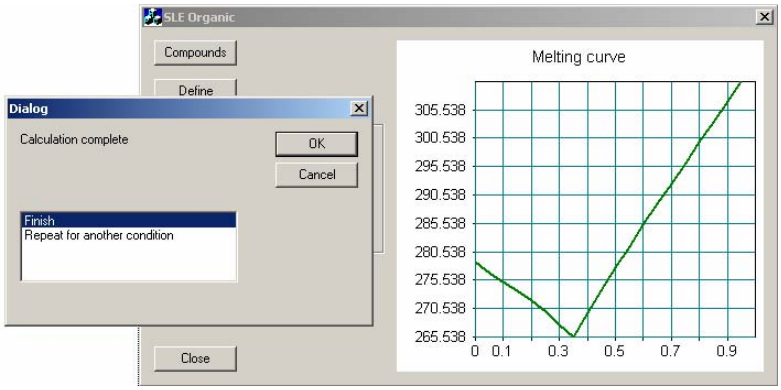
SLE-c



SLE-d



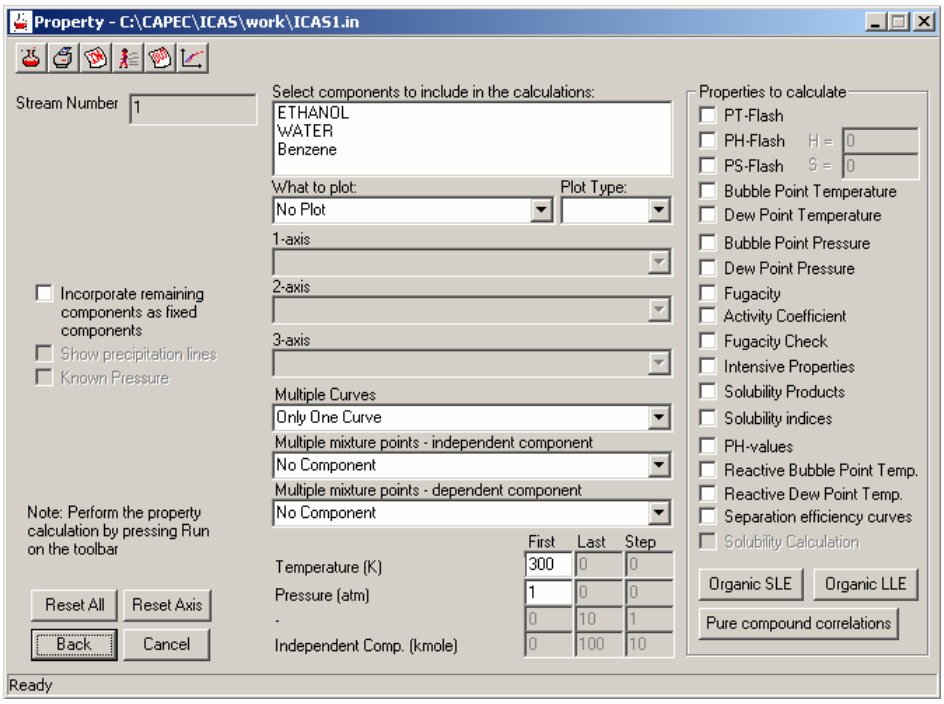
SLE-e



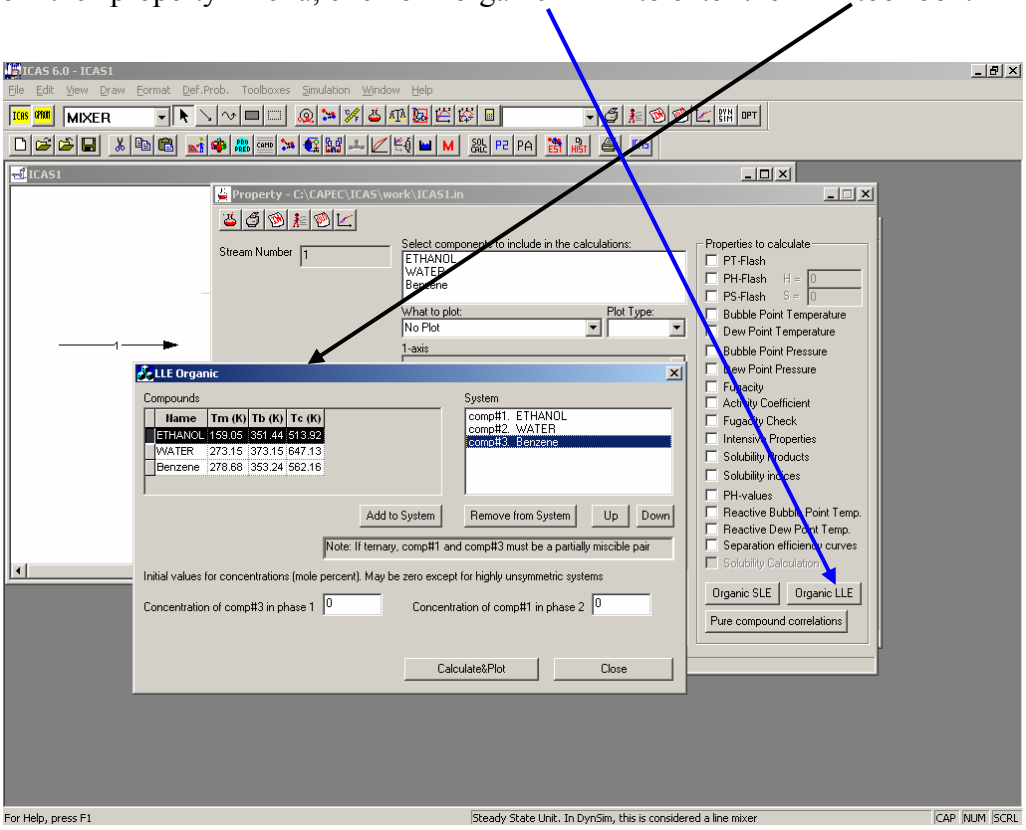
SLE-f

B2. LLE Phase Diagram

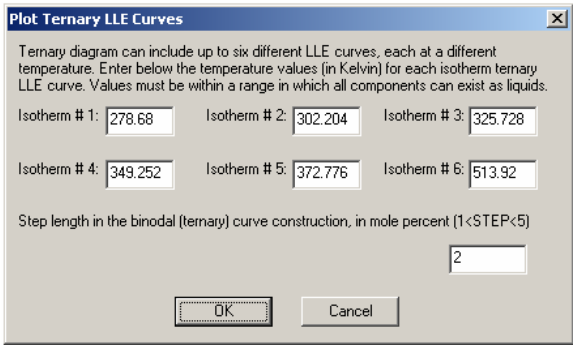
The mixture is changed to water-ethanol-benzene. The UNIFAC-LLE model is chosen and the LLE-phase diagram option is called from the ICAS-utility toolbox, as shown below.



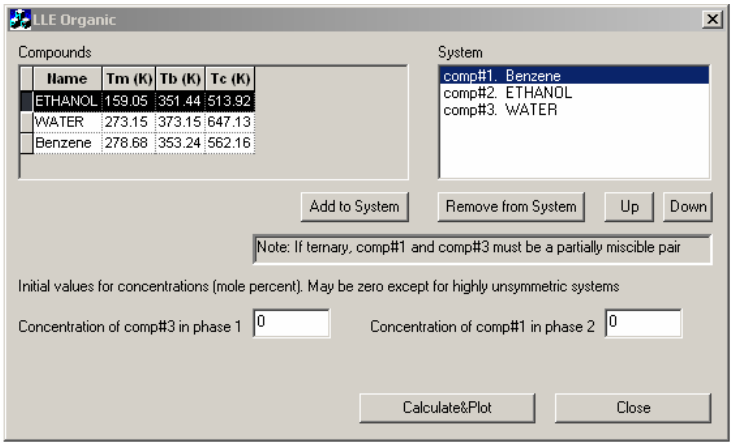
- From the “property” menu, click on “organic LLE” to enter the LLE tool-box:



- From the “LLE organic” window, click on “Calculate & Plot” to enter the “Plot Ternary LLE Curves”



- Click in OK in order to calculate a ternary LLE phase diagram:



- The calculated LLE phase diagram is shown: