ChemSep Case Book: Liquid-Liquid Equilibrium

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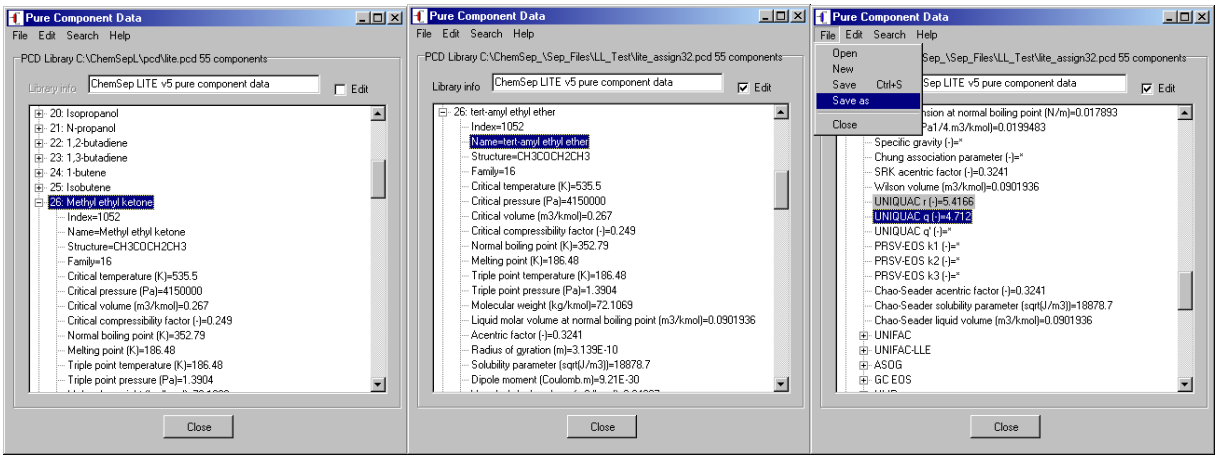
ChemSep is a program that was created in order to perform multicomponent separation process calculations. It can also be used as an aide to carrying out simple (or not so simple) phase equilibrium calculations and prepare phase diagrams. This article shows how to use ***ChemSep*** to construct liquid-liquid equilibrium diagrams for a Type I tert-amyl ethyl ether (TAEE), methanol, and water system (Arce, A., et al, J. Chem. Eng. Data, **46**, 2001, 557-561) and a Type II tert-amyl methyl ether (TAME), 1-octanol, and water system (Arce, A., Blanco M., J. Chem. Thermodynamics, **30**, 1998, 799-804). A liquid – liquid phase diagram can be constructed from the results of a number of liquid – liquid phase split calculations, an option that recently has been added to ***ChemSep***.

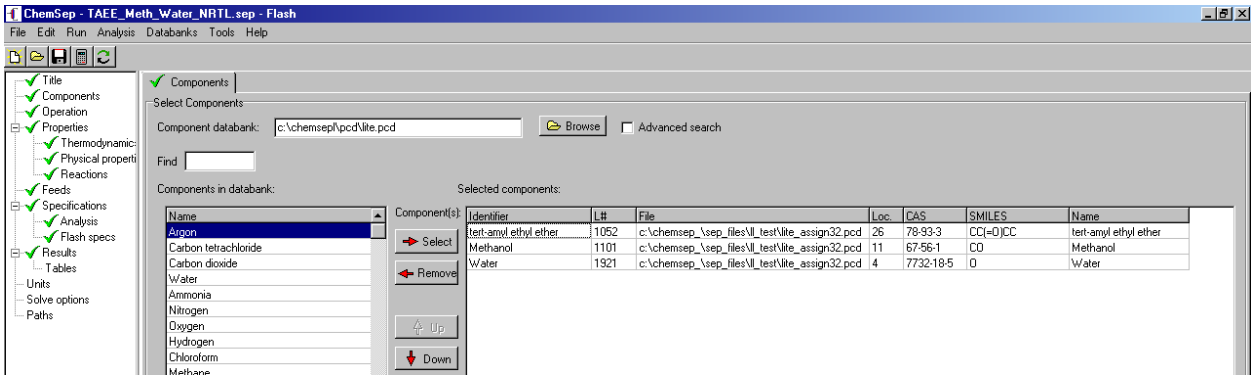
Adding/Changing Component Data

The first step of any simulation usually is to tell *ChemSep* what compounds are involved. Methanol and water are available in the databank that is part of **ChemSep-Lite** (available free from www.chemsep.com). However, TAEE is not included in the databank and it will be necessary to add the appropriate parameters so that this system can be modeled. From the *Databanks* option on the main menu of ChemSep open the databank that is to be modified. For Lite users this will be lite.pcd. Select a component that whose record will be edited to make ***ChemSep*** think that it is dealing with TAEE. In this case we select Methyl Ethyl Ketone, component number 26 in lite.pcd (left image below). For the purposes of modeling LLE in the system of interest we do not need to create a complete data record for TAEE. We need to change only the *Name* – see the center image below – so that we can recognize what component we need to select) and the UNIQUAC r and q parameters (right). In order to change anything in the databank we must first click on the *Edit* checkbox (see, again, the images below). And we must not forget to save the file when all necessary changes have been made. We recommend saving under a new name – it is all too easy to forget what component properties were *not* changed when editing a databank.



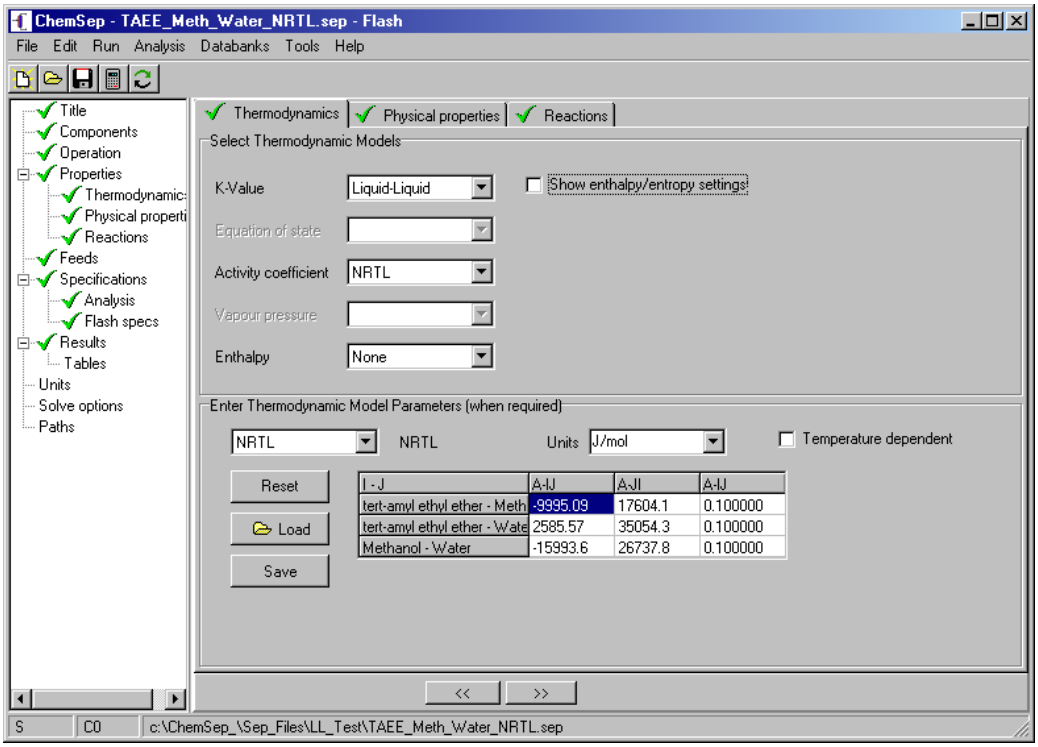
Liquid-Liquid Flash

Once the databank has been created we can select the components of interest.

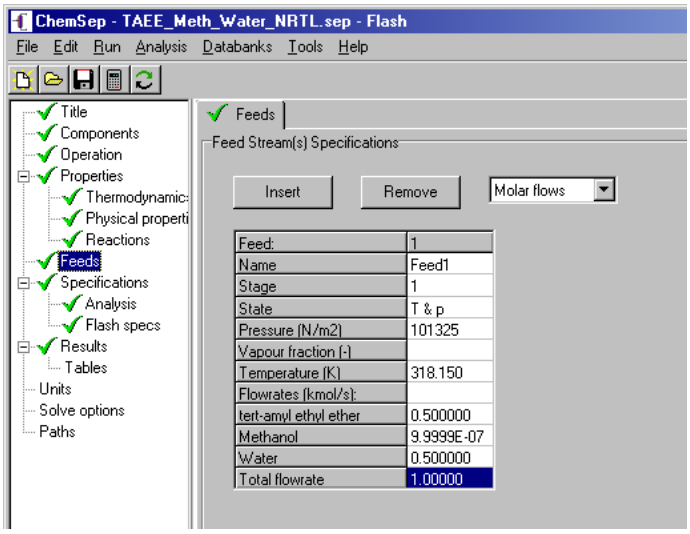


The next step is select the *Operation* – here chosen to be a simple *Flash* (screen image not shown because it is not very interesting).

Then we move to the all important selection of appropriate thermodynamic models. Here we choose the Liquid-liquid K-value model and the NRTL model for the activity coefficients. As an alternative we could select the UNIQUAC model (the parameters for both models are available in the papers cited above). The parameters are entered in the spreadsheet in the lower portion of the *Thermodynamics* panel.

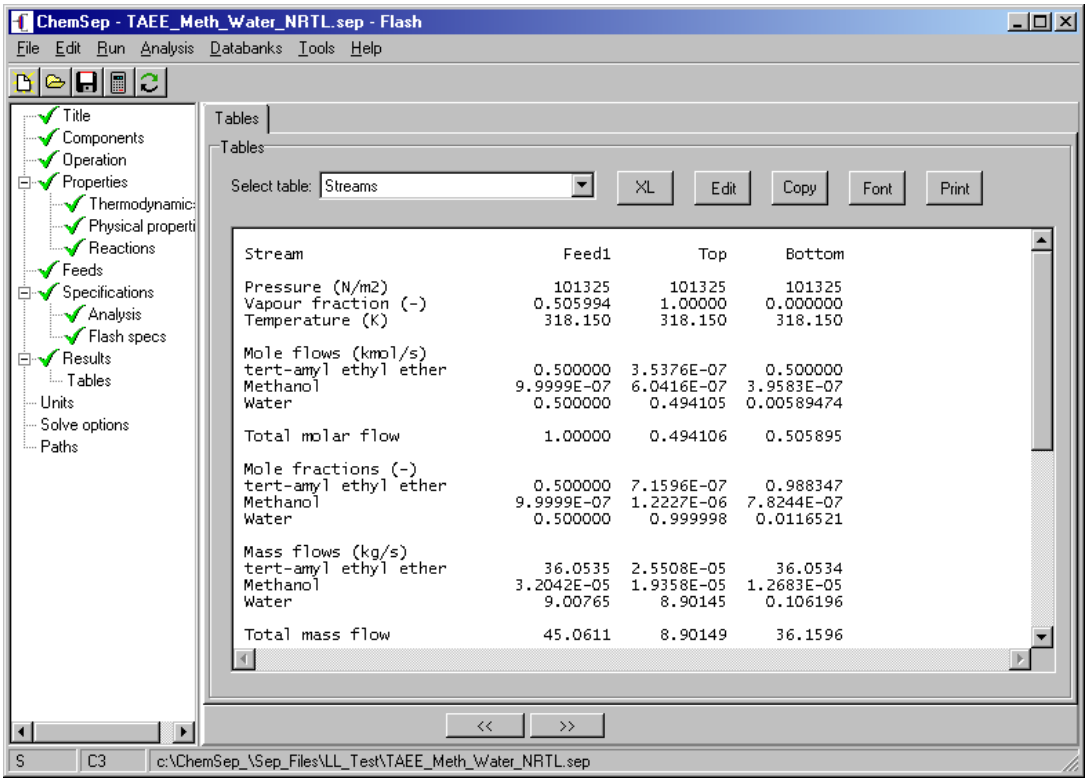


The composition of the mixture to be tested for stability is entered in the feeds panel. When constructing LL phase diagrams it is a good idea to start with a composition that is very close to an edge of a ternary triangle that represents a binary mixture that will exhibit phase separation. In this illustration that is achieved by setting the mole fraction of methanol to a very small number.



For a liquid – liquid flash we only need to specify the temperature on the *Flash Specs* panel and the problem specification is complete.

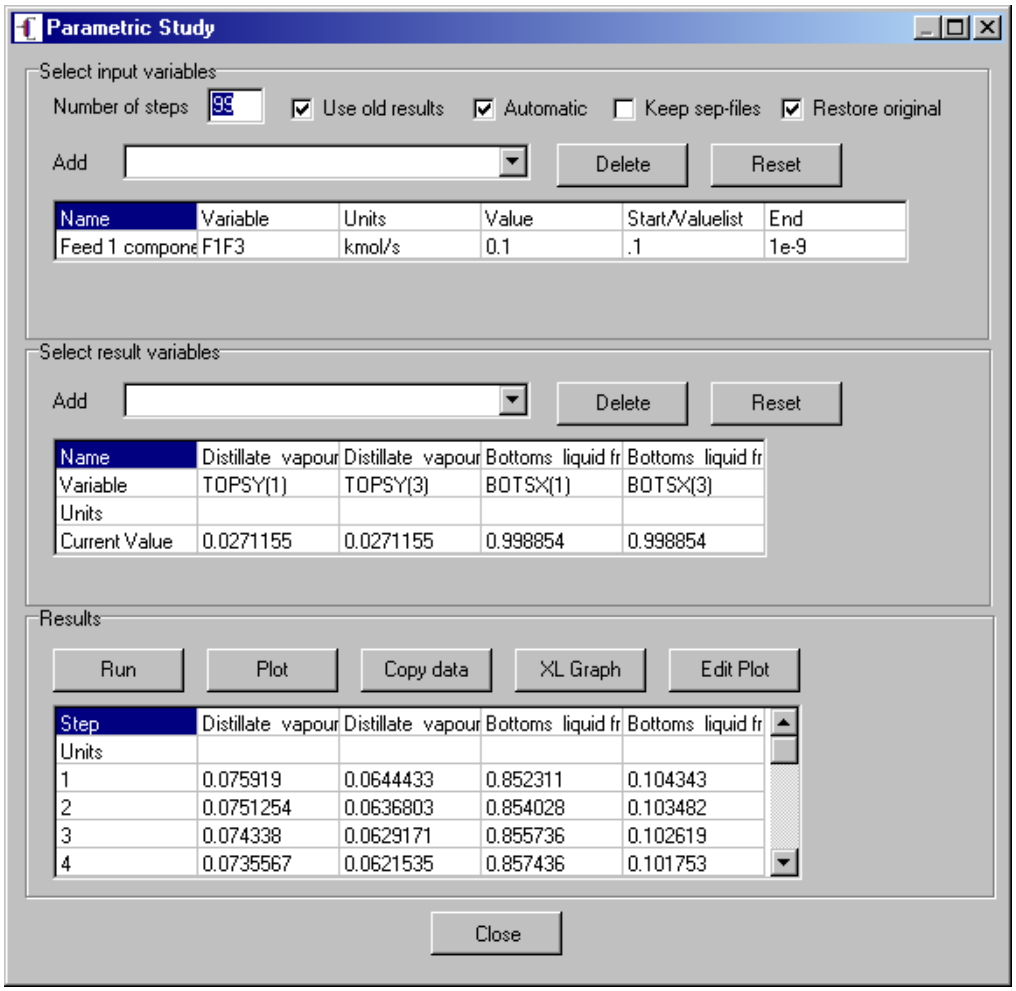
The phase split calculation is carried out by clicking on the calculator symbol that is visible in most of the screen shots shown above. The results of the calculation will be displayed on the results panel shown below:



The results of this particular calculation demonstrate that the feed composition represents a mixture that is not stable (note the different compositions for the streams labeled *Top* and *Bottom*). The mole fractions of these two streams are the ends of a single tie line on a LLE phase diagram. To construct a complete diagram we need to carry out a number of LL flash calculations. Repeating these kinds of calculation in ***ChemSep*** can be automated using the…

Parametric Study

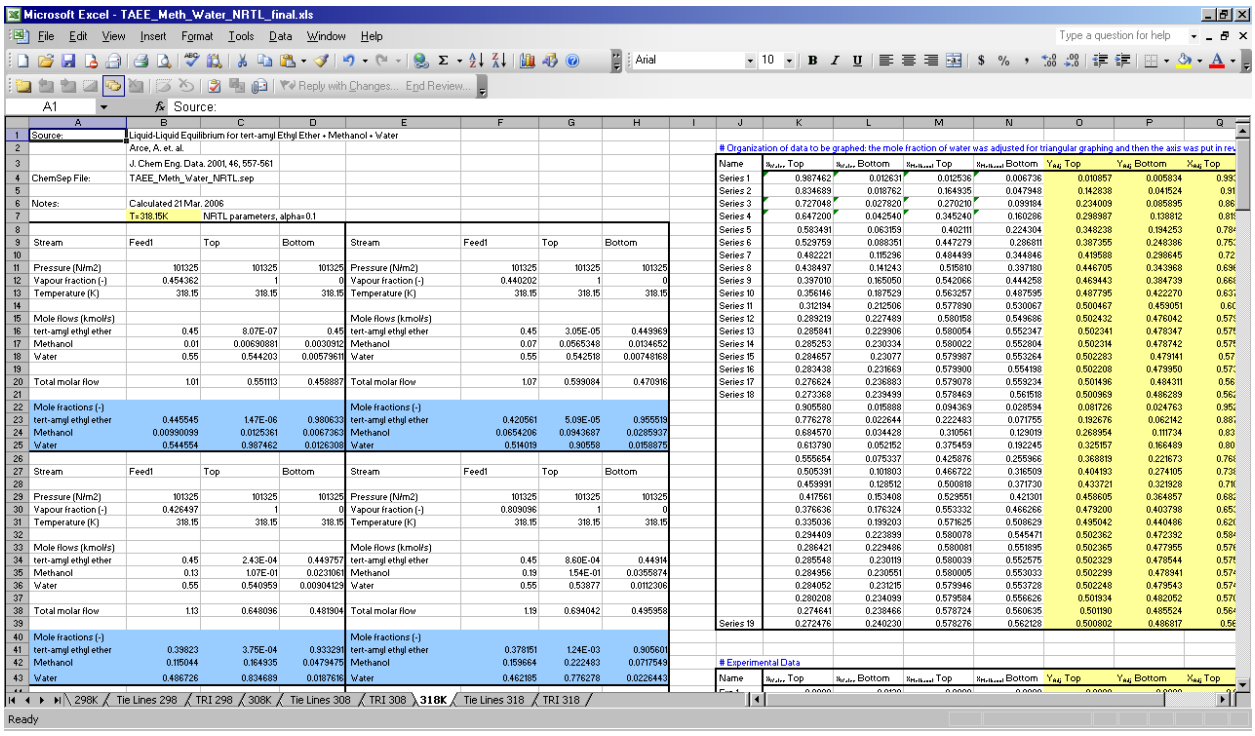
Click on the *Analysis* menu and select *Parametric Study* to bring up the window. Then add specification variables from the pull down menu to the list of parameters that will be varied. Here we have selected the amount of component 3 in the feed. In the center section we select results that we wish to monitor from another pull down list. In this illustration we have selected the mole fractions of components 1 and 3 in the product "streams" (read phases). (Disregard the reference to Distillate and Bottoms – these are just the words used internally in ***ChemSep*** to refer to the product streams.)



After we click the *Run* button ***ChemSep*** will execute 99 (see the number of steps in the top left of this screen shot) simulations at different values of the component feed flow and the selected output parameters will be tabulated in the bottom part of the parametric study panel as can be seen in the screen image shown above. This image actually is from our second illustrative example of which more below.

ChemSep also allows a parametric study with a simple list of values for the input variables; add a list of values separated by comma's or spaces in the field where normally would be specified the starting value for the input variable.

ChemSep can export the results of a parametric study to Excel, or to the plotting package provided with the program. The screen shot below shows several output tables exported to Excel and (on the right) some manipulation of the raw “data” in Excel.



The calculated compositions for the top and bottom streams were first converted into triangular (x, y) coordinates using simple geometric formulas:

$$x = x_A + \frac{x_C}{2} \qquad y = x_C\left(\frac{\sqrt{3}}{2}\right)$$

where x_A and x_C are the mole fractions of water and methanol in the Type I system and TAME and 1-octanol in the Type II system, respectively. After this adjustment, tie lines were created by connecting the top and bottom liquid equilibrium points for each feed composition. Results are shown below.

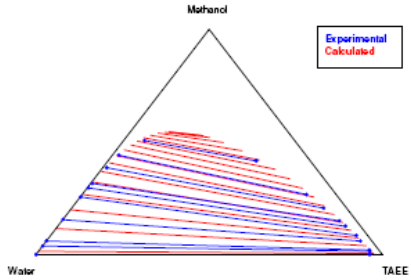


Figure 1: LLE TAEE, Methanol, and H_2O at 298.15K (UNIQUAC)

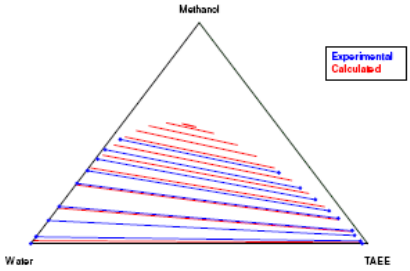


Figure 2: LLE TAEE, Methanol, and H_2O at 308.15K (NRTL; $\alpha = 0.1$)

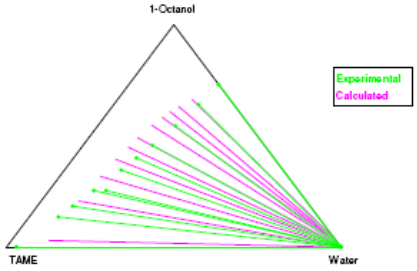


Figure 4: LLE TAME, 1-Octanol, and H_2O at 298.15 K (NRTL; $\alpha = 0.1$)

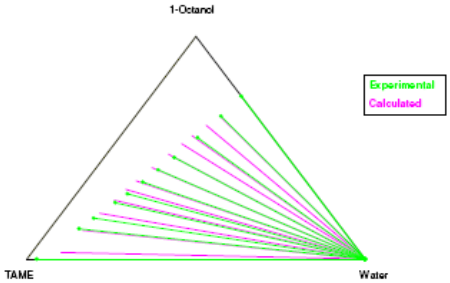


Figure 5: LLE TAME, 1-Octanol, and H_2O at 298.15 K (NRTL; $\alpha = 0.2$)

Close inspection shows that UNIQUAC model provides a slightly better fit of the Type I system at 298.15K (Figure 1), while the NRTL model better describes the systems at 308.15 (Figure 2); however, there is really little difference between the activity coefficient models at any temperature. There was more variation in the quality of the fits found for the Type II paper. As α increases the fits obtained with the NRTL model at 298.15K improve dramatically (Figures 4, 5).

ChemSep-Lite Available for Nothing!

A version of *ChemSep* with limited functionality is available for free download from www.chemsep.com/downloads/index.html. *ChemSep* Lite is limited to no more than five components, a databank with a limited number of components, no more than 50 stages in a column simulation, and no nonequilibrium model.

Availability

ChemSep is available for educational use from the CACHE corporation (www.cache.org). For licenses for non-educational use please contact the authors.

Further Information

Additional information about the program can be found at www.chemsep.com. The first author can be taylor@chemsep.com.