TERNARY VLE EXERCISE

SEC. BUTANOL-MEK-WATER DISTILLATION

PURPOSE:

Consider the possibilities for separating mixtures of 2-butanol, MEK and water with the object of purifying MEK. Demonstrate VLE regression and data analysis. Check UNIFAC predictions.

ASSUMPTIONS:

No simplifications allowed. Use only published data.

PROCEDURE:

EX1. Create a job containing the following components from the CHEMCAD physical properties data base:

1-	SEC-BUTANOL	(450)
2-	MEK	(153)
3-	WATER	(62)

From the literature we can gather the following atmospheric boiling point information (deg C):

2-3 azeotrope	-	73.86	(homogeneous)
2 (MEK)	-	79.64	
1-3 azeotrope	-	87.00	(heterogeneous)
1 (2-butanol)	-	99.54	
3 (water)	-	100.00	

In a normal distillation column with two products, we could expect to drive the products toward one or at most two of these boiling points, depending on the composition of the feed.

Set the K-value to MARG NCOR. This is a temporary measure to allow us to create binary data files for later use. We will not be using the Margules model. Using the REGRession option in UTILities, create a binary regression data file for the 1-3 binary using the data provided in EXHIBIT 1. Execute the dummy Margules regression but ignore the result. In similar fashion, create files for the 2-3 and 2-1 binaries given in EXHIBIT 2 and 3, respectively.

Reset the K-value to UNIFAC. You can now plot the three binaries (1-3, 2-3, 2-1) using UNIFAC to predict binary VLE and compare it with known data. Find the azeotrope temperatures and compositions from the numerical results which precede the plots.

TPXY REGRESSION			
Temp C	Press mmHg	X	Y
92.700	760.00	0.95000E-02	0.11600
91.000	760.00	0.16600E-01	0.21400
89.700	760.00	0.21000E-01	0.30300
89.500	760.00	0.25700E-01	0.34300
88.200	760.00	0.34000E-01	0.38700
88.000	760.00	0.43000E-01	0.38500
87.900	760.00	0.46000E-01	0.38600
88.700	760.00	0.50100	0.45200
88.700	760.00	0.51900	0.46300
89.000	760.00	0.56300	0.47000
89.700	760.00	0.60700	0.49300
89.800	760.00	0.71100	0.52000
92.100	760.00	0.81600	0.62400
94.200	760.00	0.90100	0.73100
95.800	760.00	0.96000	0.80100
97.700	760.00	0.98400	0.89800
98.400	760.00	0.99600	0.95200

EXHIBIT 1
2-Butanol / Water
VLE

TPXY REGRESSION			
Temp C	Press mmHg	X	Y
100.00	760.00	0.00000	0.00000
73.900	760.00	0.48000E-01	0.64400
73.300	760.00	0.66900	0.65800
73.400	760.00	0.73100	0.67600
73.600	760.00	0.80000	0.69700
74.000	760.00	0.84200	0.72400
74.300	760.00	0.86400	0.74800
74.800	760.00	0.88400	0.76900
75.600	760.00	0.91300	0.80800
79.600	760.00	1.00000	1.00000

EXHIBIT 2
MEK / H_2O
VLE

TPXY REGRESSION			
Temp C	Press mmHg	X	Y
99.000	760.00	0.18000E-01	0.4000E-01
97.500	760.00	0.56000E-01	0.11000
94.200	760.00	0.16400	0.29100
92.500	760.00	0.24500	0.40300
91.300	760.00	0.29100	0.45600
88.300	760.00	0.42500	0.59500
86.700	760.00	0.52100	0.67400
84.300	760.00	0.65400	0.76800
83.200	760.00	0.71700	0.81200
82.100	760.00	0.80900	0.87100
80.900	760.00	0.89200	0.96200
79.900	760.00	0.97100	0.98000

EXHIBIT 3
MEK / 2-Butanol
VLE

THE BINARY DATA TABLES USED IN THE REGRESSIONS WILL BE STORED IN THE JOB SUBDIRECTORY AS FILES NAMED AFTER THE EIGHT DIGITS DESCRIBING THE TWO COMPONENT DATABASE IDENTIFICATION NUMBERS. FOR EXAMPLE, THE THREE PAIRS IN THIS CASE ARE STORED IN FILES NAMED:

04500062	(1-3 BINARY)
01530062	(2-3 BINARY)
01530450	(2-1 BINARY)

EX2. Create a new job by copying the previous job. Change the K-value option to Wilson. Note that Wilson BIP's are already available for the 1-3 and 2-3 pairs. These BIP's are taken from the BIP library contained in the CC2 directory in a file named WILS.VLE. Enter the 1-2 (2-butanol-MEK) Wilson parameters from DECHEMA:

(Aij=567.95, Aji=-219.42)

to complete the three pairs required for the ternary system. Plot (TPXY) the three binaries and compare with DECHEMA data points at 760 mmHg. Note that even though the data points suggest that two liquid phases may exist, Wilson predicts only single phase. If you have a text editor, you can enter the Wilson parameters into the VLE library.

EX3. Create a new job by copying the previous job. Change the K-value option to NRTL. Note that NRTL BIP's are already available for the 1-2 and 2-3 pairs. These BIP's are taken from the BIP library contained in the CC2 directory in a file named NRTL.VLE. Enter the 1-2 (2-butanol-MEK) NRTL parameters from DECHEMA after dividing by 1.98721:

(Bij=-224.82, Bji=454.26, ALPHAij=.3035)

to complete the three pairs required for the ternary system. Plot (TPXY) the three binaries and compare with DECHEMA data points at 760 mmHg. If you have a text editor, you can enter the NRTL parameters into the VLE library.

The TPXY plots for the 1-3 and 2-3 azeotropes show concentration and temperature inversions in the area of the azeotropes. The NRTL model is predicting a heterogeneous azeotrope in this area, but if we use the one-liquid phase K-value method (LV), such inversions could cause numerical instability in some models. In any case, if liquid phase separation is real, a homogeneous model would give the wrong answers. Reset the K-value subcommand to LLV and replot the azeotropes. Note the difference in the curves.

IF THE MODEL MUST PREDICT IN THE REGION OF PHASE SPLITTING, THE TWO-LIQUID PHASE OPTION SHOULD BE INVOKED.

EX4. Create a new job by copying the previous job. Change the K-value option to UNIQ. Note that UNIQ BIP's are already available for the 1-2 and 2-3 pairs. These BIP's are taken from the BIP library contained in the CC2 directory in a file named UNIQ.VLE. Enter the 1-2 (MEK-2-butanol) UNIQ parameters from DECHEMA:

(Uij-Ujj = -241.97, Uji-Uii = 387.07)

to complete the three pairs required for the ternary system. Plot (TPXY) the three binaries and compare with DECHEMA data points at 760 mmHg. If you have a text editor, you can enter the UNIQ parameters into the VLE library.

The TPXY plots for the 1-3 and 2-3 azeotropes show concentration and temperature inversions in the area of the azeotropes. The UNIQ MODEL is predicting a heterogeneous azeotrope in this area, but if we use the one-liquid phase method, such inversions could cause numerical instability in some models. In any case, if liquid phase separation is real, a homogeneous model would give the wrong answers. Reset the K-value subcommand to LLV and replot the azeotropes. Note the difference in the curves.

IF THE MODEL MUST PREDICT IN THE REGION OF PHASE SPLITTING, THE TWO-LIQUID PHASE OPTION SHOULD BE INVOKED.

EX5. As an exercise in binary regression, create a new job by copying the previous job and regressing the DECHEMA VLE data for the 1-3 pair using the WILSON model. Binary regression does not capture and use binary parameters it finds in the BIP table.

First, determine if the parameters available in the BIP table represent a converged set for the data regressed. Run the regression with minimum and maximum parameter values set to the BIP table values. Check the model fit with a TPXY plot.

Repeat the exercise with default conditions on the two parameters. Compare the parameters and fit with those above.

Repeat the exercise using UNIFAC to regress WILSON parameters. Compare parameters and fit with those above.

EX6. Create a new job by copying the previous job. Use topology or graphics to create an LLVF flash module with LATEnt heat enthalpy and the following input stream:

INPUT STREAM TO LLV

2-BUTANOL	0.24 MOLES
MEK	0.36 "
WATER	0.40 "
Temperature	25 deg C
Pressure	760 mmHg

Set the LLVF as follows:

MODE	=	2
PAR 1	=	0.00001 (V/F)
PAR 2	=	760 mmHg

Execute the LLVF and view the streams using the mole fraction option and check against DECHEMA ternary data displayed as EXHIBIT 4. Note how well binary VLE parameters match ternary data.

EX7. Create a new job by copying the previous job. Create new WILSON parameters by regressing DECHEMA data. Note that in the case of VLE TERNARY regression, the parameter estimates are taken from the BIP table. Compare the regressed parameters with those developed from the binaries.

Execute the LLVF and view the streams **using the mole fraction option** and check against DECHEMA ternary data.

Note how well ternary VLE parameters match ternary data. You should find that the ternary model will fit better.

VLE TERNARY REGRESSION					
Press mmHg	Temp C	X1	X2	Y1	Y2
760.00	78.411	0.18100	0.72000	0.90000E-01	0.68900
760.00	76.739	0.16000	0.64000	0.95000E-01	0.62100
760.00	76.139	0.14000	0.56000	0.72000E-01	0.58300
760.00	76.050	0.12100	0.47000	0.68000E-01	0.55300
760.00	76.200	0.10100	0.39000	0.63000E-01	0.53600
760.00	79.372	0.50000E-02	0.20000E-01	0.57000E-01	0.50000
760.00	82.700	0.40000E-02	0.16000E-01	0.56000E-01	0.37500
760.00	81.461	0.36200	0.53900	0.19100	0.62000
760.00	79.289	0.32100	0.48000	0.17800	0.53000
760.00	78.472	0.28100	0.42000	0.14600	0.49200
760.00	78.439	0.24000	0.36000	0.13300	0.45700
760.00	78.178	0.20000	0.30000	0.10900	0.45000
760.00	78.572	0.16000	0.24000	0.10700	0.44000
760.00	82.450	0.11000E-01	0.15000E-01	0.95000E-01	0.35000
760.00	85.089	0.90000E-02	0.11000E-01	0.80000E-01	0.35200
760.00	84.661	0.54200E	0.35900	0.30700	0.43800
760.00	82.189	0.48300	0.32000	0.26400	0.42400
760.00	81.878	0.42200	0.28000	0.24000	0.36300
760.00	81.239	0.36000	0.24000	0.21100	0.35000
760.00	81.178	0.30000	0.20000	0.20400	0.35400

EXHIBIT 4

2-Butanol / MEK / Water

VLE