UNIVERSITY OF SOUTH CAROLINA
ECHE 460 CHEMICAL ENGINEERING LABORATORY I

ETHANOL/WATER VAPOR-LIQUID EQUILIBRIUM USING AN OTHMER STILL

Prepared by:

Professors M. A. Matthews and J. A. Ritter

Department of Chemical Engineering
Swearingen Engineering Center
University of South Carolina
Columbia, SC 29208

Revised: January 2001

1. Introduction

In order to design a piece of separation equipment such as a distillation column, modern chemical engineering practice relies on computer-aided design routines. These routines solve the design equations (which you learn in ECHE 322 and ECHE 440) and contain the various thermodynamic models needed to describe liquid-phase and vapor-phase non-idealities (which you learned about in ECHE 311). Typically at low pressures, liquid phase non-idealities are modeled with an activity coefficient model (e.g. Wilson equation, UNIFAC, UNIQUAC, NRTL, and other which are described in your textbooks). Vapor phase and non-idealities are always modeled with an equation of state (Redlich-Kwong, Soave, or Peng-Robinson, for example). Inevitably, any vapor phase equation of state of state or liquid phase activity coefficient model contains empirical (a.k.a. "fit to experimental data") parameters. Part of the marketing of a computer process simulation package such as ASPEN is the extent of its thermodynamic parameter data base. Big simulators have a lot of built-in data. Sometimes, however, parameters for certain chemical mixtures are missing, or perhaps the built-in parameters do not accurately model the actual process. In such cases it is necessary for the chemical engineer to obtain his or her own experimental data and do a regression analysis to obtain more reliable parameter values. The binary VLE experiment in ECHE 460 is intended to teach you how to obtain your own binary parameters for a simplified thermodynamic model.

An important device used to obtain binary vapor-liquid equilibrium data is the Othmer Still or one of its variations. The equilibrium is obtained by establishing a closed loop system with the recirculation of the cooled condensed vapor phase. This recirculation allows the compositions of the liquid and vapor phases to come to equilibrium such that the vapor phase leaving the heated liquid is of equivalent composition with the condensed vapor phase being returned. Equilibrium has been reached when the temperature of the vapor phase is constant similar to a T-x-y diagram. The Othmer paper is attached for additional references.

2. Objectives

The objectives of this experiment are to obtain some experimental measurements of VLE for the ethanol/water system to verify literature data. Also, you will fit your results with various models, and will employ a thermodynamic consistency test to evaluate the quality of your data.

3. Operating Procedure

1. Prepare a water/ethanol mixture, which is approximately 95 per cent by weight. The TA will ready the apparatus by turning on the cooling bath to approximately 10°C. Verify that the stopcocks on the still are closed.

2. Transfer your mixture into the still through the filling neck. DO NOT pour the solution in through the thermometer port.

3. Place the plug in the filling neck and remove the thermometer and adapter.

4. Plug in the heating coil and heat until the air has been driven out of the still. (Approximately 5-8 minutes.)

5. Replace the thermometer and adapter.

6. Allow the condensate to fill the receiver the first time and then empty the receiver throwing away this portion properly.

7. Continue heating the solution until the thermometer gives a steady vapor temperature reading for three minutes. (This should take from 15-30 minutes.)

8. Having reached equilibrium you now take samples from both the boiling flask and receiver. Allow these to cool to room temperature and analyze via the DMA 48 densitometer. Refer to the attached procedure for the density meter. Calibration data will be provided.

9. Unplug the heating coil, drain all remaining fluids, and rinse the still with water.

10. Repeat steps 2 through 9 until all sufficient data have been obtained. Determine an appropriate number of samples to describe the VLE curve, and discuss the number of experiments with your TA.

4. Analyzing Experimental Vapor-Liquid Equilibrium Data

Begin with the criterion for phase equilibrium and make a few assumptions. For a binary vapor-liquid equilibrium state the criterion for phase equilibrium is:

$$\bar{f}_i^L = \bar{f}_i^V \qquad\qquad i = 1,2 \qquad\qquad (1)$$

The fugacities are broken into several contributions each for the sake of analysis.

$$\text{(liquid)} \qquad \bar{f}_i^L = x_i \gamma_i \phi_i^{sat} P_i^{sat} \exp\left(\int_{P_i^{sat}}^{P} \frac{V_i^L}{RT} dP \right) = y_i \phi_i^V P = \bar{f}_i^V \qquad\qquad (2)$$

Now one can make some reasonable assumptions to simplify this equation. First of all, the Poynting factor, $\left(\exp\left(\int_{P_i^{sat}}^{P} \frac{V_i^L}{RT} dP \right) \right)$, is the effect of pressure on the fugacity of a pure liquid. It is usually close to unity for low pressures. Another good assumption at low pressures is that the fugacity coefficient of the pure saturated liquid is near unity, as well as the fugacity coefficient of each species in the mixture. Certainly the ratio of the fugacity coefficients will be near unity. Thus we can rearrange the criteria for phase equilibrium as follows:

$$x_i \gamma_i P_i^{sat} \frac{\phi_i^{sat}}{\phi_i} \exp\left(\int_{P_i^{sat}}^{P} \frac{V_i^L}{RT} dP \right) = y_i P \qquad (3)$$

Let $\dfrac{\phi_i^{sat}}{\hat{\phi}_i^{v}} = 1$ and $\exp\left(\int_{P_i^{sat}}^{P} \dfrac{V_i^L}{RT} dP \right) = 1$; then equation 3 simplifies to

$$x_i \gamma_i P_i^{sat} = y_i P \qquad (4)$$

In your experiment the pressure of the VLE experiment was near 1 standard atmosphere so the assumptions and simplifications made above are valid. In your experiment you measured phase densities and converted these to the vapor and liquid phase mole fractions (x_i and y_i). You also recorded the pressure and temperature. Because the temperature is known you can calculate or look up the vapor pressure of each pure species at the experimental temperature. Thus you can calculate the activity coefficient directly from the data.

After doing this for all the experimental compositions one has a table of experimental data (isobaric, non-isothermal data for the apparatus you are using). The last step is to use these data to fit the needed parameters in an activity coefficient model. The Wilson, NRTL, UNIFAC, and other models are fairly complicated and the regression of model parameters requires non-linear analysis. For this experiment we recommend that you examine one or two simpler models, the Van Laar or the Margules equations. The algebra in these models is readily accessible to undergraduate students. However, these models are not used in most real process simulators because these models are restricted to binary systems only. Because practically all chemical processing involves three or more components, a real-life design would require one of the more complicated models.

The Van Laar model is as follows; it has two parameters (α and β):

$$\ln \gamma_1 = \frac{\alpha}{\left[1 + \dfrac{\alpha}{\beta} \dfrac{x_1}{x_2} \right]^2} \qquad \ln \gamma_2 = \frac{\beta}{\left[1 + \dfrac{\beta}{\alpha} \dfrac{x_2}{x_1} \right]^2} \qquad (5)$$

One way to get the parameters is to do some algebra on Equation (5) and isolate α and β. This would give a one-point estimate of the parameters because you use only the activity coefficients at a single composition. Because you have several different compositions you can generate a set of parameters $\{\alpha\}$ and $\{\beta\}$ at each experimental data point. Usually it is assumed that the parameters vary with temperature and because your data are non-isothermal this may be the best approach.

There is another way to treat the data, that is, assume that the parameters do not depend strongly on temperature and regress all of the data simultaneously to get the coefficients. The temperature range in your experiments was not very great and this is probably a decent assumption. (It is possible with a different apparatus to obtain isothermal, non-isobaric data and this treatment would therefore be exact.) In order to do simultaneous regression it is helpful to

linearize the model equations and then do linear regression. (You learned how to linearize equations in ECHE 300 using the book by Felder and Rousseau; you have been doing linear regression for a long time). The linearized for of the Van Laar equation is as follows:

$$\sqrt{\ln \gamma_1} = \sqrt{\alpha} - \sqrt{\frac{\alpha}{\beta}} \sqrt{\ln \gamma_2}$$

Thus, you plot $\sqrt{\ln \gamma_1}$ versus $\sqrt{\ln \gamma_2}$ from the experimental data: the slope of the line is $-\sqrt{\frac{\alpha}{\beta}}$ and the intercept is $\sqrt{\alpha}$. (How can you tell is the Van Laar is a good model over the entire temperature/composition range?) Always plot the data according to the model you use and examine the expected behavior. NEVER just use the regression coefficients without examining the quality of the fit!

The same type of analysis can be done with the Margules equation. The Margules equation is

$$\ln \gamma_1 = \left[A + 2(B - A)x_1\right]x_2^2 \qquad \ln \gamma_2 = \left[B + 2(A - B)x_2\right]x_1^2$$

The single-point estimate of the two Margules constants is

$$A = \frac{x_2 - x_1}{x_2^2}\ln \gamma_1 + 2\frac{\ln \gamma_2}{x_1} \qquad B = \frac{x_1 - x_2}{x_1^2}\ln \gamma_2 + 2\frac{\ln \gamma_1}{x_2}$$

The linearized form of the Margules equation is

$$\frac{\ln \gamma_1}{1 - x_1} + \frac{\ln \gamma_2}{x_1} = A + (B - A)x_1$$

Another way to estimate activity coefficients is using the Wilson model. The Wilson model is as follows:

$$\ln \gamma_1 = -\ln\left(x_1 + \Lambda_{12}x_2\right) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right]$$

$$\ln \gamma_2 = -\ln\left(x_2 + \Lambda_{21}x_1\right) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right]$$

where

$$\Lambda_{12} \equiv \frac{v_2}{v_1}\exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right)$$

5

$$\Lambda_{21} \equiv \frac{v_1}{v_2} exp\left(-\frac{\lambda_{12} - \lambda_{22}}{RT}\right)$$

v_1 and v_2 are the liquid molar volumes of the respective pure components; in this case, ethanol (1) and water (2). Also $\lambda_{12} - \lambda_{11} = a_{12} = 382.3$ cal/mole and $\lambda_{12} - \lambda_{22} = a_{21} = 955.45$ cal/mole. This is a measure of the interaction energy between the molecules of 1 and 2.

5. **Data Analysis and Reporting:**

1. Compute and plot the following:
   A. x-y diagram
   B. T-x-y diagram

2. Calculate and plot experimental γ_1 and γ_2 versus x_1 for both components on the same graph. Use these to extrapolate to the infinite dilution activity coefficients. Also, examine the graphs and discuss whether they appear as expected.

3. Plot $\ln\left(\frac{\gamma_2}{\gamma_1}\right) = f(x_i)$ versus x_i over the complete composition range from $x_1 = 0.0$ to $x_1 = 1.0$

   and integrate the area under the curve. The areas under the curve on either side of $\ln\left(\frac{\gamma_2}{\gamma_1}\right) = 0$ should be equal. This is a well-known test of *thermodynamic consistency.* Research and derive this equation and state the assumptions. (See, for example, the texts by Walas or Smith, Van Ness, and Abbott.)

4. Using the Wilson equation and the set of interaction parameters given to you from the literature, compare these calculated activity coefficients with the experimental data. Plot a point-to-point comparison of γ_{lit} and γ_{exp}, i.e., use the experimentally determined temperature (T) at each point. Then try an average temperature $\left(T_{ave} = \frac{T_{b,H2O} + T_{b,EtOH}}{2}\right)$, predict a range of γ_{Tave} found from $y_i = 0 \rightarrow 1$ (20 points). Can T_{ave} be used as a good approximation?

5. Obtain model parameters for the Van Laar and Margules equations by fitting the linearized forms of the equations. Plot the activity coefficients obtained from the fit to the Van Laar and the Margules equations. How well do the models fit the experimental data?

6. Compare your data to reliable data from the literature.

6. <u>References</u>

Walas, Stanley M.

Smith, J.M, Van Ness, H.C., Abbott, M.M.

Othmer, D.F. *Analytical Chemistry*, Vol. 20, No. 8, pp. 763-766 (August 1948).

7. <u>Procedure for measuring density:</u>

The compositions of the vapor and liquid phases will be determined indirectly by measuring their densities in the liquid phase at a known temperature. Comparing these densities with a calibration table of densities at known compositions will allow the unknown vapor and liquid compositions to be interpolated.

Densities will be measured with a DMA 48 digital density meter. The operating principles are described in the attached materials. The meter must me calibrated with air and with deionized (DI) water in order to obtain the best possible precision and accuracy.

<u>Starting Procedures:</u> Refer to the operating manual for additional details. Turn on the DMA 48. Change the measurement temperature to 30 ^{o}C by pressing **F300** ↵ and then the temperature **30** ↵. When the instrument temperature stabilizes, the symbol × will cease flashing.

The oscillator tube must be cleaned and dried before either calibrating or performing density measurement on an unknown sample. To do this, use a clean syringe to inject clean DI water through the oscillator tube, followed by clean acetone. After the acetone is injected, turn the pump on (the switch is on the front panel) and blow out the remaining acetone. This will dry the oscillator.

<u>Calibration with air and DI water</u>: The DMA 48 must be calibrated at each measurement temperature. This is done using air and DI water after the oscillation tube is cleaned and dried. First establish the measurement temperature, 30 ^{o}C, as explained above. Then press **F100** ↵. The display will show the calculated density of air corresponding to 30 ^{o}C and the prevailing atmospheric pressure (check the local barometric pressure). The symbol × will be displayed and the units **g/cm^3** will flash until the instrument (the oscillation period) stabilizes. To display the oscillation period, press ↵. When the oscillation period stabilizes, the density measurement will likewise be stabilized. You can alternate the display between the density value and the oscillation period.

After calibration with air, perform calibration with DI water. Turn on the light switch (found on the front panel of the DMA 48). Slowly inject the oscillator with DI water, making sure there are no air bubbles in the oscillator. Fill the oscillator completely (beyond the mounting points) and then turn the light off so that the instrument can maintain the correct measurement temperature. Press **F101** ↵. The display will show the calculated density of water at 30 ^{o}C

(verify that the temperature has stabilized). The symbol × will be displayed and the units **g/cm³** will flash until the instrument stabilizes. When the instrument has stabilized, the display will show **dev B** (the difference between the present value of the calibration constant B and the value from the most recent prior calibration). The symbols **dev B** and × will be on but not flashing. If **dev B** is less than or equal to 0.005 (or for the very first calibration **dev B** is between 1.3 and 1.6) then press ↵. If not, clear the calibration table by pressing **CLR** and start over. If density measurements are to be made at more than one temperature, then the instrument must be calibrated with air and DI water at each temperature.

Densities of unknown mixtures: The oscillator tube must be cleaned and dried. Use a syringe to load the unknown sample slowly into the oscillator tube. About 0.7 ml is required. Use the light to ensure that there are no air bubbles in the sample. Filling is complete when the sample has passed from the thin part to the thick part at the opposite end of the oscillator. Leave the syringe in position after filling. Turn off the light, confirm that the measurement temperature is stable, and begin the density measurement. To obtain the density measurement, press **F505** and read the density from the display. Press **F500** to read the period of oscillation.

To remove the sample from the oscillator, turn on the pump. After the sample is removed, flush and dry the oscillator using DI water and acetone as described above. The oscillator is then ready for a new unknown sample mixture.

If it is desired to obtain readings at other temperatures, press **F300** ↵ and enter the new temperature.   Always ensure that the instrument temperature and oscillation period have stabilized before recording density data. Return the temperature to 30 °C when all measurements are completed.