CHEG 345-011

Isothermal Vapor Liquid Equilibrium Analysis of the Binary Systems Containing Methyl-Acetate, Acetone, and Methanol

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Abstract

In this work, the vapor-liquid equilibrium behavior of a ternary solution of methyl acetate (MeOAc), acetone (DMK), and methanol (MeOH) is indirectly evaluated under isothermal conditions at 75 °C. This was completed through calculating infinite dilution activity coefficients through measuring the relationship between pressure and mole fraction near the infinite dilution limit of solute for the MeOH-MeOAc and DMK-MeOAc binary systems. These calculated infinite dilution activity coefficients for the MeOAc(1)-MeOH(2) system are: $\gamma_1^\infty = 2.08 \pm 0.06$ and $\gamma_2^\infty = 2.51 \pm 0.06$, while for the MeOAc(1)-DMK(2) system are: $\gamma_1^\infty = 1.10 \pm 0.03$ and $\gamma_2^\infty = 2.27 \pm 0.06$. These infinite dilution activity coefficient values were used to extrapolate the behavior of the full binary systems using the Van Laar and Wilson models, which showed close agreement. They indicated maximum pressure azeotropes present in both systems at MeOAc mole fractions of 0.643 for the MeOAc-MeOH binary and 0.597 for MeOAc in the MeOAc-DMK binary. Addition of infinite dilution activity coefficients of the third binary mixture allowed for extrapolation of the ternary system, revealing a maximum pressure ternary azeotrope at 2.08 bar, at a composition of 0.125, 0.563, and 0.312 mole fraction for DMK, MeOAc, and MEOH, respectively which agrees with the previous literature.[1]

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Introduction

Understanding of vapor liquid equilibrium (VLE) is essential in adequate design of separation systems, specifically distillation columns. These columns are often extremely energy demanding, consuming 50 to 70% of all energy used in the chemical manufacturing business[2]. Distillation columns use a series of trays where VLE is achieved, separating compounds due to their relative volatilities. In this work, the VLE behavior of two binary systems, methanol - methyl acetate and acetone - methyl acetate, are extrapolated under isothermal conditions at 75 °C through determining infinite dilution activity coefficients. Literature values for the third binary, methanol - acetone, are then used to determine the behavior of the ternary system of these three components. All of these compounds are common industrial solvents; therefore knowledge of how to separate a mixture of them, may be important if they are contaminated with one another.

Background

Phase equilibrium in a mixture is achieved when the temperature, pressure, and chemical potential is uniform. This occurs when the fugacity is equal in each phase for each component. Which in the case of vapor liquid equilibrium (VLE) is given by equation (1) below.

$$\overline{f_i^L}(T,P,\underline{x}) = \overline{f_i^V}(T,P,\underline{y})$$

(1)

In VLE, assuming the Lewis-Randall rule, this occurs when the conditions in equation (2) are met for each component. Where γ_i is the activity coefficient of the species in solution, ϕ_i is the pure species fugacity coefficient, x_i is the liquid mole fraction, and y_i is the vapor mole fraction. Without assumption of the Lewis-Randall rule the fugacity coefficient used must be that of the species in the appropriate mixture, but this assumption is valid in all low pressure systems.

$$x_i\gamma_i^L(T,P,\underline{x})P_i^{vap}\phi_{sat,i}exp\left(\frac{V_i^L[P_{total} - P_i^{vap}(T)]}{RT}\right) = y_iP_{tot}\phi_i^V$$

(2)

In low pressure systems, the Poynting pressure correction and the ratio of the fugacity coefficients can be neglected. Such that equation (3) applies.

$$x_i\gamma_i^L(T,P,\underline{x})P_i^{vap}(T) = y_iP_{tot}$$

(3)

In the binary systems under analysis this assumption would introduce ~1% error, as discussed in Appendix A. Due to the introduction of a relatively small amount of error, this criteria for VLE will be used. Therefore, to predict VLE behavior a model for how the activity coefficient varies with liquid mole fraction must be known. The activity coefficient is the exponential of the excess Gibbs free energy over the quantity of the gas constant times temperature. Since various expansions for the excess Gibbs free energy exist, so do various activity coefficient models. The parameters of these models can be determined if the infinite dilution activity coefficients are known. Under isothermal conditions this can be calculated using equation (4).

$$\gamma_1^\infty = \frac{P_2^{vap}(T) + \left(\frac{\partial P_{tot}}{\partial x_1}\right)_{T,x_1 \to 0}}{P_1^{vap}(T)}$$

(4)

After calculating the infinite dilution activity coefficient using equation (4), parameters can be found to model the activity coefficients for the full binary system, as will be done for the van Laar and Wilson models. Through using equation (3), full system VLE behaviour can then be obtained.

Objectives

The objective of this experiment was to characterize the VLE behavior of a ternary mixture of acetone, methanol, and methyl acetate under isothermal conditions at 75 °C. To do this the infinite dilution activity coefficients are calculated from experimental data of pressure over mole fraction near infinite dilution for the binary mixtures of methanol - methyl acetate and acetone - methyl acetate. Literature values for the third binary, methanol - acetone, can then be used in conjunction with the ternary van Laar model to predict full ternary system behavior.

Experimental Methods

Apparatus

Figure 1 shows the apparatus used to conduct the experiment. The apparatus was equipped with a circulating water bath, the temperature of which can be controlled by mixing cold and hot water streams, and a convection oven to control temperature to ensure isothermal behavior. Each of these two temperature regulating systems is monitored by two K-type thermocouples each. Within this isothermal system, there are two "cells" one reference and one sample that are kept at the set temperature, recorded again by a K-type thermocouple. The reference cell has only ever contained pure solvent, while in the sample cell solute is also injected into the previously pure solvent throughout the course of the experiment. The absolute pressure of one of these cells is then recorded as well as the differential pressure between them. Six of these apparatuses were used in this experiment, four to measure the pressure dependence at infinite dilution of each end of the binary systems and two to measure the temperature dependence of vapor pressure for methyl acetate and acetone.
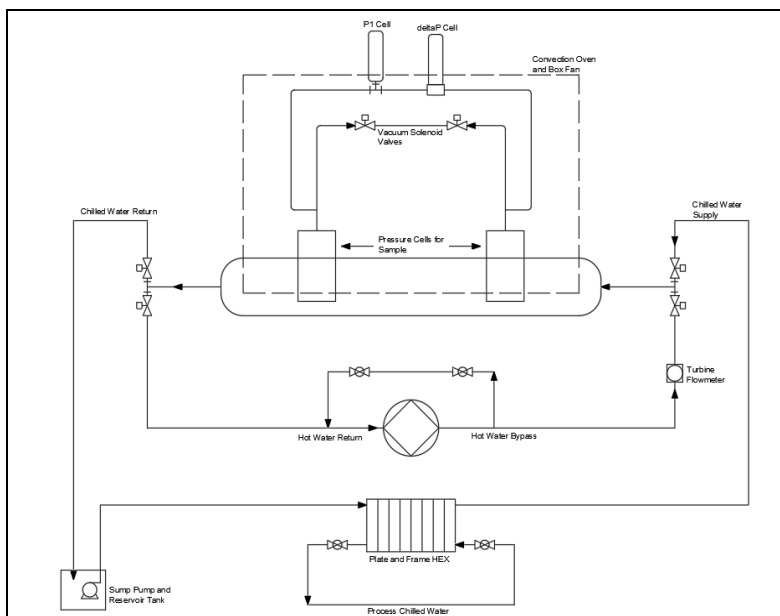
Figure 1: Experimental apparatus for isothermal VLE measurements.

Materials

Physical properties of compounds in this analysis are given in Table 1 below, as well as the purities available.

Table 1: Important physical properties of components in the system from the literature. Values come from the NIST webbook of each substance [3] and [4] for MeOAc critical properties.

compound	T_{bp} (K)	T_c (K)	P_c (bar)	P_{vap}(75 °C) (bar)	Purity (%)
methanol	333.8 ± 0.3	513 ± 1	81. ± 1	1.508	≥99.9
acetone	329.3 ± 0.3	508 ± 2	48 ± 4	1.853	99.9
methyl acetate	330 ± 0.9	506.8	46.9	1.895	≥99.8

Safety Hazards

Proper protective equipment including splash goggles, gloves, and lab coats were worn by all members for the entirety of the lab. The lab's safety showers and eyewash stations were located before the lab began, as any exposure would require fifteen minutes of rinsing the infected area. All chemical species were disposed of in their proper receptacle. Syringes were handled with care with all lab members aware of what the person with the syringe was doing at any point in time. Care was also taken not to contact the apparatus while it was running as contacting the 75 ℃ apparatus would cause burns. Similarly, care was taken to restrict the presence of all sparks in

the labs, due to the flammable nature of all of these components. More information on the specific precautions taken for each individual chemical is available in Appendix B.

Design of Experiment

From equation (4) accurate knowledge of the pressure dependence of mole fraction near infinite dilution is necessary to determine the infinite dilution activity coefficients. This pressure dependence was to be modeled with a quadratic fit, as it provides enough fitting power to determine the curvature of pressure with respect to mole fraction near infinite dilution, without introducing excessive fitting parameters. Therefore, preliminary calculations were made using the infinite dilution activity coefficients calculated by the UNIFAC model, obtained from Aspen plus[5], to determine limiting mole fractions in which this quadratic fit did not introduce systematic error greater than the error in the pressure sensors (±0.001 bar). These values are provided in Table 2 below, the amount of solute injected was then chosen to be well within this range.

Table 2: Limiting mole fractions where quadratic fit does not introduce systematic error.

Binary	Solute	Aspen (γ^∞)	limiting mole fraction
Methanol - Methyl acetate	Methanol	2.60	0.13
	Methyl acetate	2.43	0.15
Methyl acetate - Acetone	Methyl acetate	1.1	0.2
	Acetone	1.32	0.18

Procedure

For all units, prior to starting the experiment, the ambient pressure of the absolute pressure sensor and ambient temperature of each thermocouple was recorded. Pure solvent was then massed and then loaded into the reference and sample cell of each unit.

For the four units used to measure binary system behavior, syringes were loaded with enough solute to reach a limiting mole fraction smaller than that given in Table 2 in five equal injections. The amount of solute injected was verified gravimetrically through weighing the syringe after adding the solute. The syringe was then mounted within the experimental apparatus. The convection heater and recirculating water bath were then turned on and, once coming to equilibrium at 75 °C, the temperature and pressure were recorded. Then, a fifth of the solute in the syringe was injected by a mechanical plunger. Once the solution re-equilibrated, the pressure and temperature were measured again. This was repeated until the syringe was emptied, at which point it was removed and re-weighed, to determine the exact mass of solute injected.

In the two units that only contained solvent, vapor pressure readings were obtained through recording absolute pressure of solvent after said solvent had equilibrated at a variety of temperatures.

Results and Discussion

Prior to analyzing the experimental data, the pressure sensors and thermocouples were calibrated. More detail is given in Appendix C, but briefly, the ambient pressure readings were compared to the estimated barometric pressure at the time of sealing the vessels; however, no major deviations were found necessitating extra calibration. The ambient temperature of the room was then determined through backing out the deviation in the set of thermocouples that measured the vapor pressure of acetone, the purest solvent available. This ambient temperature was then used to correct all of the thermocouples' readings through finding their deviation at ambient conditions. This experimental data is then given in Appendix D, which also includes a plot of pressure over time, indicating that no abnormal injection occurred. Finally, Appendix E contains sample calculations for all equations used in the following analysis.

Data Reduction of Vapor Pressure Correlations

To determine the infinite dilution activity coefficient, as given in equation (4), accurate measurements of the vapor pressures of both solvent and solute are needed at the temperature of interest. To determine this, one isothermal VLE unit was dedicated to measuring the vapor pressure of methanol and another the vapor pressure of methyl acetate. Figure 2 depicts the pressure measurements, after they were converted from psia to bar, and plotted over the average corrected temperature of all thermocouples.
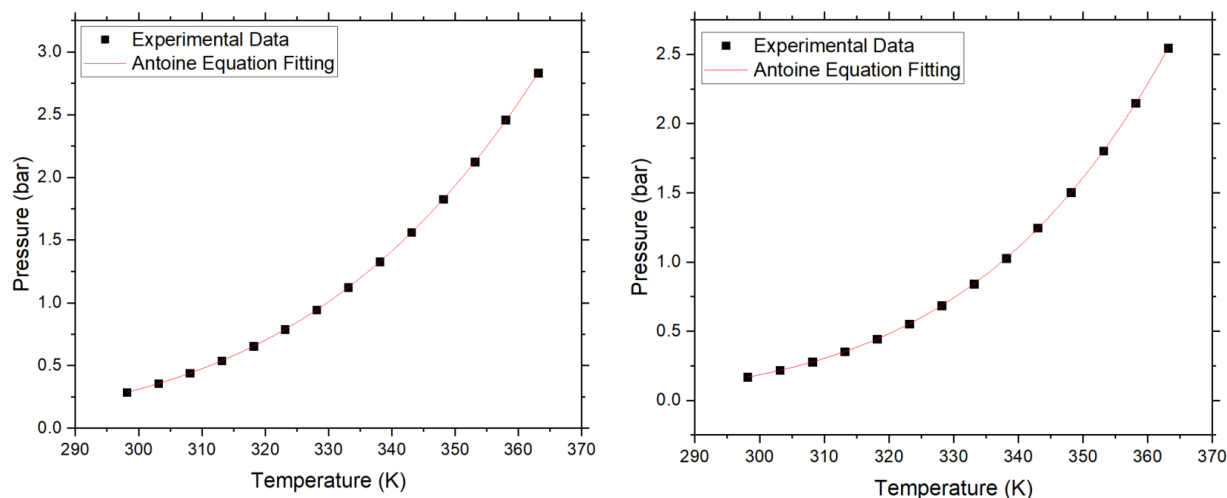

Figure 2: Vapor pressure regression for methyl acetate (left) and methanol (right).

These plots were then fit to the antoine equation for vapor pressure given in equation (5) below, where P is the absolute pressure in bar. The residuals for these fits are presented in Appendix F indicating that this equation does fit the data well, minus one outlier in each curve.

$$log_{10}(P) \ = \ A \ - \ \frac{B}{C+T} \tag{5}$$

The parameters for these fits are given in Table 2 below, as well as the vapor pressure when evaluated at 75 °C. Note that the full regressed parameters were used in these calculations, with the error and rounding added after. A correlation from the NIST webbook for acetone is also provided.

Table 3: Antoine equation parameters and vapor pressure

Compound	A	B	C	Pvap(75 °C) (bar)
Methyl Acetate	4.07 ± 0.87	1090 ± 40	-62 ± 5	1.83 ± 0.05
Methanol	5.11 ± 0.09	1520 ± 60	-39 ± 5	1.51 ± 0.03
Acetone	4.42448	1312.253	-32.445	1.8531

As expected due to the high correlation in the fit and normally distributed residuals, the vapor pressure calculated using this correlation matches the measurement at the nominal temperature of 75°C of 1.82601 ± 0.00002 bar methyl acetate and 1.50346 ± 0.00002 bar for methanol.

Binary VLE Behavior of Methanol and Methyl Acetate

Before predicting the VLE behavior of this system using activity coefficient models, the infinite dilution activity coefficients must be determined. As evident from equation (4), knowledge of the change in pressure over mole fraction of component in interest must be known at the infinite dilution limit. To determine this, the pressure of the binary was plotted over the liquid mole fraction, given in Figure 3. In doing so, it is assumed that the liquid mole fraction is equal to that injected into the cell, as the volatility of the compounds under analysis are similar, indicating that a similar proportion of each compound will be present in the vapor phase as in the liquid phase. This means that there will be no substantial deviation from the mole fraction in the liquid phase between that injected into the cell.
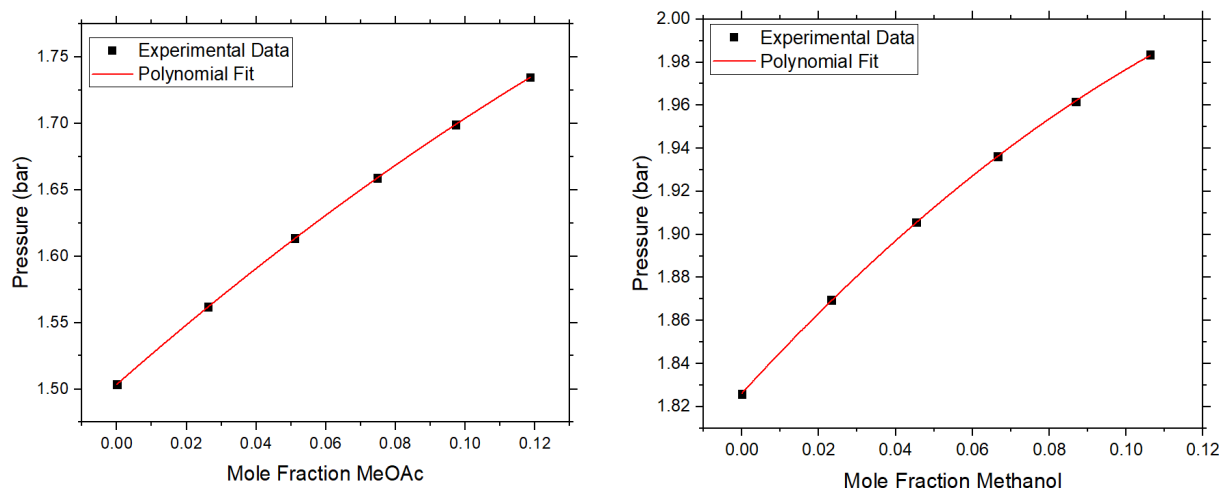
Figure 3: Pressure over mole fraction for (left) methyl acetate in methanol and (right) methanol in methyl acetate.

Both plots in Figure 3 were fit with quadratics, to determine the dependence of pressure on mole fraction of solute at infinite dilution. The equation for the fit for methyl acetate in methanol is given in equation (6) and for methanol in methyl acetate in equation (7), where P is the pressure in bar and x_1 is the mole fraction of the solute.

$$P = (-2.97 \pm 0.04) \times x_1^2 + (2.300 \pm 0.005) \times x_1 + (1.5035 \pm 0.0001) \quad (6)$$

$$P = (-4.4 \pm 0.1) \times x_1^2 + (1.94 \pm 0.01) \times x_1 + (1.8267 \pm 0.0003) \quad (7)$$

Residual analysis in Appendix F shows that these fits are evenly distributed around zero, indicating that they fit the data well.

Using these equations for pressure near the infinite dilution limit of solute, the derivatives of these equations were taken and calculated when the solute concentration was zero. This was then plugged into equation (4) as shown in Appendix E to find that the infinite dilution activity coefficient of methyl acetate in methanol is 2.08 ± 0.06 and that the infinite dilution activity coefficient of methanol in methyl acetate is 2.51 ± 0.06. Note that these values were calculated using the average temperature of the corrected thermocouples, as given in Appendix D of 74.92 °C for both systems.

These values are similar to, but not exactly the same as those given by the UNIFAC model simulated by Aspen of 2.42 for methyl acetate in methanol and 2.6 for methanol in methyl acetate.[3] This could be due to errors in the recorded pressures or temperatures, as will be discussed further in the error analysis section of this report. Though, deviations are also expected with the UNIFAC model as it is purely predictive, so it should not be expected to perfectly predict these coefficients.

Using these infinite dilution activity coefficients, one can then determine the parameters for any two constant activity coefficient models to extrapolate the behavior of the full binary system. We choose to compare the behavior of the van Laar and the Wilson model, as the van Laar model assumes random solution behavior while the Wilson model does not. The van Laar activity coefficient model is given in equation (7) below for component 1, where α and β are the two model constants.[5]

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

(8)

To obtain the activity coefficient of component 2 one can switch α and β and 1 and 2 in equation (9). From these equations one can see that the natural logarithm of the infinite dilution activity coefficient of what one defines as component 1 is equal to α, and that of 2 is equal to β.

The Wilson model for the activity coefficient of component 1 is given by equation (9) below, where A12 and A21 are the fitting parameters.[5]

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

(9)

Similar to the van Laar model, the activity coefficient of component 2 can be obtained by switching 1 with 2 within the negative natural logarithm term and mole fraction multiplying the bracketed term with the negative mole fraction of component 1.

MATLAB code was written to solve for the parameters of these models and iteratively determine the pressure in which VLE is achieved for a series of liquid mole fractions. This was completed through solving for the pressure in which equation (3) is true, knowing the vapor and liquid mole fractions must sum to one. This treatment allows one to both plot pressure over the liquid and vapor mole fractions of one component, known as a P-x-y plot, and the mole fraction of a component in the vapor phase over the mole fraction of said component in the liquid phase, known as a x-y plot. This was completed for the methanol - methyl acetate binary in Figure 4.
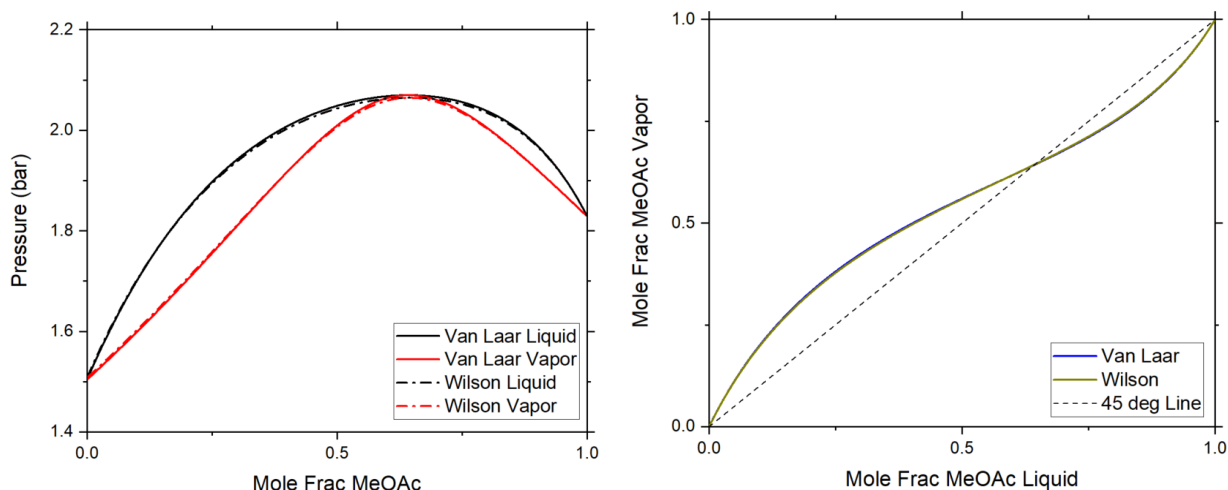
Figure 4: Pressure over mole fraction methyl acetate (left) and mole fraction methyl acetate in the vapor phase over that in the liquid phase (right), for the methanol-methyl acetate system.

Figure 4 shows good agreement between the van Laar and Wilson models in both the P-x-y and the x-y plots, indicating that the assumption of random vs non-random molecular distribution does not dramatically impact this analysis. Only a very slight deviation can be seen in these models in the P-x-y plot with the Wilson model predicting a slightly lower maximum pressure than the van Laar model. While the x-y plot shows essentially identical behavior.

From the P-x-y plot in Figure 4, it is evident that the methanol - methyl acetate binary contains a maximum pressure azeotrope. This maximum pressure occurs near 2.1 bar, which is within the range in which the low pressure assumption applies with reasonable error, as discussed in Appendix B. Similarly, the x-y plot shows clearly that this azeotrope occurs at a mole fraction of methyl acetate of 0.643, as this is where the model predictions intersects at the 45 degree line.

Binary VLE Behavior of Acetone and Methyl Acetate
Similar analysis can then be completed for the results of the acetone - methyl acetate binary system. For this system, the pressure over mole fraction near infinite dilution is given in Figure 5, along with their associated quadratic fits.
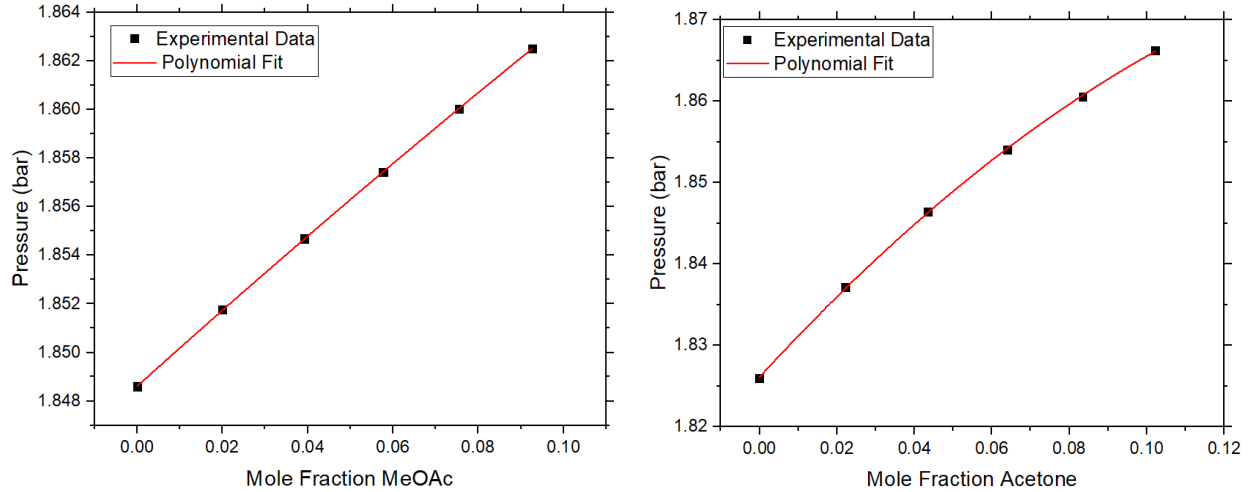
Figure 5: Pressure over mole fraction for (left) methyl acetate in acetone and (right) acetone in methyl acetate.

The equations for these linear fits are given in equation (10) for methyl acetate in acetone and equation (11) for acetone in methyl acetate.

$$P = (-0.0863 \pm 0.009) \times x_1^2 + (0.1579 \pm 0.0009) \times x_1 + (1.84861 \pm 0.00002)$$

(10)

$$P = (-1.24 \pm 0.06) \times x_1^2 + (0.516 \pm 0.007) \times x_1 + (1.8613 \pm 0.0001)$$

(11)

These quadratic fits again well represent data, as can be seen in the residuals provided in Appendix F and the small errors in the fitting constants.

These expressions can be used, again in conjunction with the vapor pressure data in Table 3 and equation (4), to find the infinite dilution activity coefficients. Using this method, infinite dilution coefficient of methyl acetate in acetone was determined to be 1.10 ± 0.03 and the infinite dilution activity coefficient of acetone in methyl acetate to be 1.27 ± 0.06. Note that these values were calculated using the average temperature of the corrected thermocouples, as given in Appendix D of 74.91 °C when MeOAc was the solute and 74.90 when methanol was the solute.

Note that these values are in agreement with those predicted by UNIFAC of 1.1 for methyl acetate in acetone and 1.32 for acetone in methyl acetate, indicating that the predictive model well predicts this system.

Using these values, as described for the methanol - methyl acetate system, P-x-y and x-y plots can be created using the van Laar and Wilson models. These plots were constructed using the same MATLAB program, and are present in Figure 6 below.
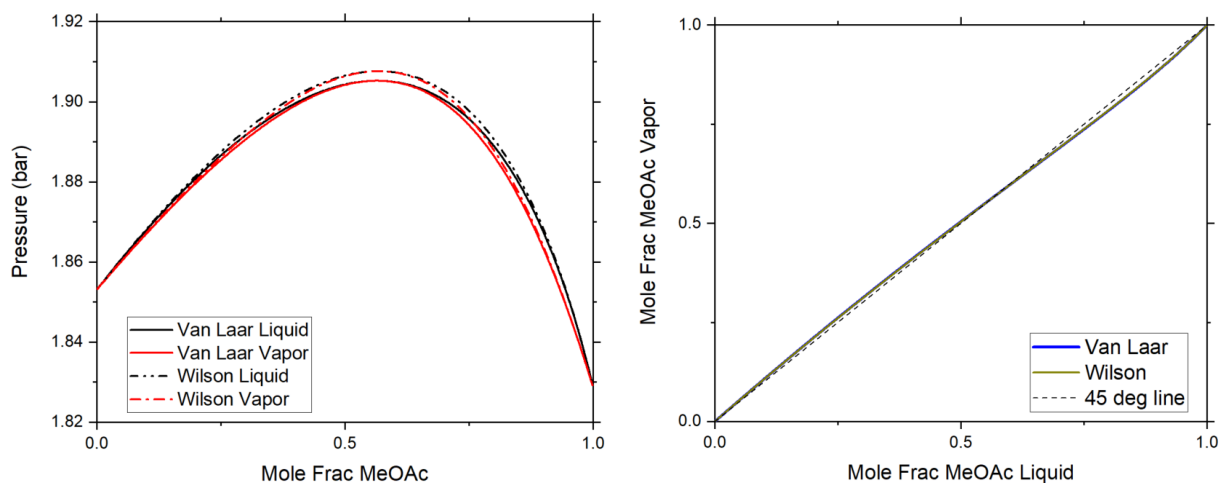
Figure 6: Pressure over mole fraction methyl acetate (left) and mole fraction methyl acetate in the vapor phase over that in the liquid phase (right), for the acetone -methyl acetate system.

Figure 6 again demonstrates good agreement between the van Laar and Wilson models for this system, as only a slight deviation in them can be seen near the maximum pressure system. Again, this indicates that the assumption of random distribution vs uniform distribution does not make a difference in this binary.

Like the methanol-methyl acetate system, it is evident from the P-x-y plot in Figure 6 that the acetone-methyl acetate binary contains a maximum pressure azeotrope. This maximum pressure occurs near 1.91 bar, which is within the range where the low pressure assumption applies with reasonable error. From the intersection of the x-y plot one can see that this azeotrope occurs when the mole fraction of methyl acetate is approximately 0.567.

It is notable that due to the similarities between these compounds that the x-y plot almost perfectly follows the 45 degree line, indicating that the vapor and liquid mole fractions are very similar throughout the binary system, in contrast to that of the other binary mixture. Because of this, these compounds would be virtually impossible to separate using distillation, as the number of stages necessary in a distillation column needed would be extremely large.

Ternary System Analysis
The behavior of the combined ternary system of methanol, methyl acetate, and acetone was then evaluated. To do so, the infinite dilution activity coefficients of methanol in acetone and acetone in methanol were pulled from the literature. Specifically, Wilask et al.[6] provide a correlation for the temperature dependence of the van Laar parameters of this binary system, which can be used to determine the infinite dilution activity coefficients. Using this correlation, the infinite dilution

activity coefficient for methanol in acetone at 75 °C is 1.677 and for acetone in methanol 1.810. These values compare reasonably with those determined by UNIFAC of 1.79 for methanol in acetone and 1.84 for acetone in methanol.

Ternary system behavior can then be predicted by using the ternary van Laar activity coefficient model. This is given in equation (12) below for component 1, where the equations for the activity coefficient of component 2 can be obtained by replacing all 1s with 2s and vice versa, while the same can be done for component 3 by replacing all 1s with 3s and vice versa.[5]

$$ln(\gamma_1) = \frac{\left[x_2^2 A_{12} \left(\frac{A_{21}}{A_{12}}\right)^2 + x_3^2 A_{13} \left(\frac{A_{31}}{A_{13}}\right)^2 + \frac{x_2 x_3 A_{21} A_{31}}{A_{12} A_{13}} \left(A_{12} + A_{13} - \frac{A_{23} A_{12}}{A_{21}} \right) \right]}{\left[x_1 + x_2 \left(\frac{A_{21}}{A_{12}}\right) + x_3 \left(\frac{A_{31}}{A_{13}}\right) \right]^2}$$

(12)

Each of the six infinite dilution activity coefficients can then be used to back out one of the parameter constants (A_{ij}). Once this is completed, a script similar to that described for the binary system can be created, where the mole fraction in the liquid phase is set and pressure iterated until equation (3) is met for all components and mole fractions of vapor and liquid each sum to one. This was completed for a wide range of liquid mole fractions, with solutions of constant pressure and $k_i = 1$ captured. Where k_i is the ratio of mole fraction in the vapor phase to that in the liquid phase. These lines of constant $k_i = 1$ must intersect at the azeotrope of a solution, as at the azeotrope the mole fraction in the liquid and vapor phases are equal for all components.

The results of this iteration can then be presented in ternary plots. Specifically, Figure 7 provides isobars for this system.
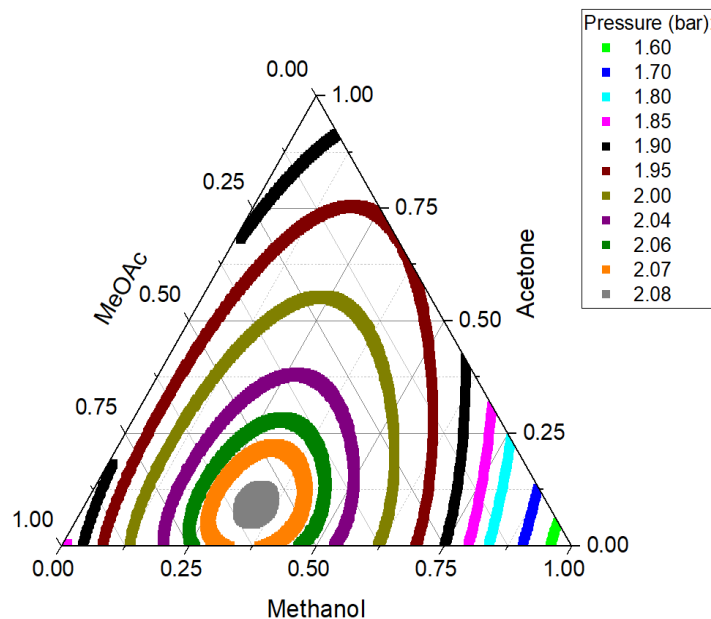
Figure 7: Ternary plot for constant isobars for the acetone, methyl acetate, and methanol system.

From Figure 7 it is apparent that the pressure increases as one approaches the lower middle section of the plot, nearing higher concentrations of methyl acetate. Specifically, there is a maximum pressure azeotrope near 2.08 bar, similar in pressure to that of the methanol - methyl acetate system. This azeotrope is located in a similar position to that identified by Severns et al.[1] for the same system.

Figure 8 provides a representation of those mole fractions of constant $k_i = 1$ for each component.
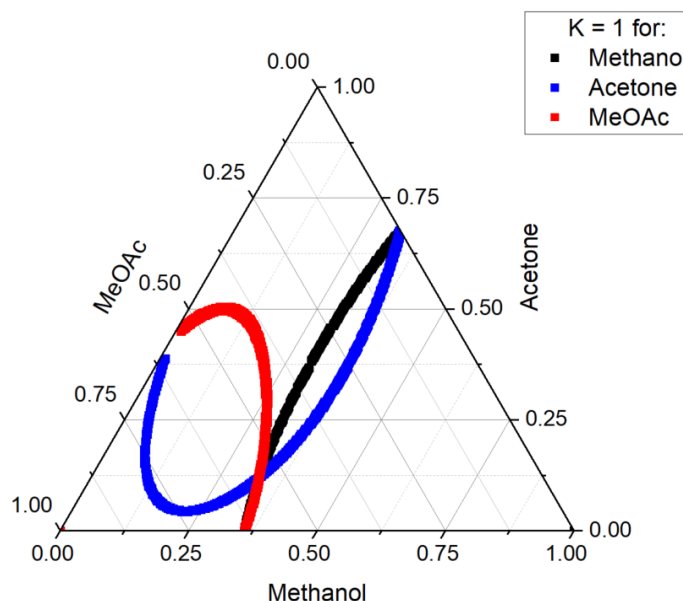

Figure 8: Ternary plot for constant $K_i = 1$ for the acetone, methyl acetate, and methanol system.

Figure 8 also confirms the presence of the ternary azeotrope specifically near a mole fraction of acetone of 0.125, mole fraction of methyl acetate at 0.563, and a mole fraction of methanol at 0.312, as this is the intersection of all three lines. The intersection of these lines at the infinite dilution limit of one component represent the binary azeotropes, which are present in all systems. Note that the red and blue lines for acetone and methyl acetate should intersect, as expected from Figure 6, but do not in this representation due to limitations in the iteration method used to save computational time.

Error and Sensitivity Analysis
To determine how systematic error, or that error which is constantly biased in one direction, would impact the calculated infinite dilution activity coefficients, sensitivity analyses were completed to see the impact of slight biases in temperature and dP/dx_1. The dependence on

temperature was first evaluated using equation (4) with the same dP/dx_1 but with the vapor pressures evaluated over a range of ± 1 °C, a deviation significantly higher than the error expected from each thermocouple of 0.02 °C.

Table 4: Estimates of the sensitivity of the activity coefficient to temperature through recalculation of vapor pressures in eq (4), assuming no change in infinite dilution pressure.

Temp (°C)	γ^∞ DMK in MeOAc	γ^∞ MeOAc in DMK	γ^∞ MeOAc in MeOH	γ^∞ MeOH in MeOAc
74	1.277	1.100	2.562	2.113
74.5	1.273	1.099	2.534	2.095
75	1.269	1.097	2.506	2.078
75.5	1.265	1.096	2.479	2.062
76	1.261	1.094	2.452	2.046

Notice that even large temperature variations do not dramatically impact the values for the infinite dilution activity coefficient past the average uncertainty of these values of ± 0.06. For example, given that the temperature corrections for the thermocouples were very small, if the experiment were actually run at 74.5°C rather than 75°C, there is less than a 1% difference between the γ^∞ values.

A similar analysis was performed for the value of dP/dx_1 and its effect on the resulting activity coefficient. In this case the value of dP/dx_1 was changed by ± 2% at constant 75 °C to isolate how sensitive the infinite dilution coefficient is to a systematic bias in this measurement. The results of this analysis, shown in Table 5, are similar to the conclusion reached for temperature changes.

Table 5: Estimates of the sensitivity of the activity coefficient to pressure through recalculation of infinite dilution pressure slope in eq (4), assuming no change in temperature.

Change in dP/dx	γ^∞ DMK in MeOAc	γ^∞ MeOAc in DMK	γ^∞ MeOAc in MeOH	γ^∞ MeOH in MeOAc
-2%	1.263	1.095	2.481	2.054
-1%	1.266	1.096	2.493	2.066
0%	1.269	1.097	2.506	2.078
1%	1.272	1.098	2.519	2.091

	2%	1.274	1.099	2.532	2.104

Again, values for the activity coefficients varied again by less than 1% for 2% changes in the value for dP/dx_1. This analysis was performed in order to determine how systematic errors in the pressure sensors may impact the infinite dilution activity coefficient. However, it is possible that a systematic bias in pressure readings would not result in change in shape of the plot, only the absolute values. Regardless, one can still see that slight variations in the fit would not dramatically increase error.

However, solvent purity may impact this slope and contribute to overall systematic error as well. This impact can be evaluated knowing that the purites for the acetone, methyl acetate and methanol are $\geq 99.9\%$, $\geq 99.8\%$, and 99.9% respectively, on a mass basis. Assuming that this impurity is water, the largest percent difference in solute composition can be evaluated, the results are shown in Table 6. A sample calculation is given in Appendix F.

Table 6: Change in composition, accounting for the purity of solvents and solutes.

Solvent	Solute	Largest % Difference in Mole Fraction of Solute
MeOAc	Acetone	1.55%
Acetone	MeOAc	0.40%
MeOAc	MeOH	1.54%
MeOH	MeOAc	0.54%

Table 6 implies that using methyl acetate as the solvent produced the largest error due its purity being as low as 99.8%. However, the maximum percent correction of 1.55% still does not produce a large difference in the calculation of the infinite dilution activity coefficients. Using the "corrected" composition data to regress the pressure/mole fraction data, $\gamma^\infty = 1.274$ was calculated for acetone in methyl acetate. This is the largest variation we see in the activity coefficient due to impurities and yet it is still less than a <1% difference in the original value, within the confidence interval. While the methyl acetate could be more pure, the correction accounting for water as the impurity produces a negligibly small change in our calculations.

From this sensitivity analysis, small amounts of systematic bias in this experiment are unlikely to change the calculated infinite dilution activity coefficients dramatically. Whereas, random error was mostly minimized by taking a wide range of measurements for each data point and using

precise instruments, minimizing the amount of random fluctuations. This indicates that the reported values for infinite dilution activity coefficients are accurate.

Conclusions

Pressure over mole fraction of solute at infinite dilution measurements were made near infinite dilution at a constant temperature of nominally 75 °C for the methyl acetate - methanol and methyl acetate - acetone systems. Vapor pressure measurements over temperature were also made for pure methyl acetate and methanol regressing antoine parameters for each component. These gave vapor pressures of 1.83 ± 0.05 bar for methyl acetate and 1.51 ± 0.03 bar for methanol at the temperature of interest. These values were then used to regress infinite dilution activity coefficients. Finding that the the infinite dilution activity coefficient is 2.08 ± 0.06 for methyl acetate in methanol and 2.51 ± 0.06 for methanol in methyl acetate, 1.10 ± 0.03 for methyl acetate in acetone, and 2.27 ± 0.06 for acetone in methyl acetate. Sensitivity analysis showed that these values are not significantly impacted by systematic error much greater than that predicted possible by the calibration, introduced by the thermocouple, pressure sensor, or impurities in the compounds. Indicating that these values are accurate.

The low pressure form of the condition for vapor liquid equilibrium, equation (3) was then used to extrapolate the behavior of the full binary system. This assumption was made as the errors associated with it, as described in Appendix A, were small. The Wilson and Van Laar models were then used to predict the full pressure vs mole fraction behavior, using the calculated infinite dilution factors to find the fitting parameters. These two models were in agreement with each other and can be taken as reasonable models for the binary P-x-y plots, both predicting maximum pressure azeotropes in the same location. Literature data was used for infinite dilution activity coefficients of methanol-acetone binary mixtures in order to predict the ternary phase behavior of the three components. This ternary system behavior was predicted using the ternary van Laar activity coefficient model which showed a maximum pressure azeotrope at 2.08 bar.

Recommendations

There are several ways that this experiment could be improved to record more accurate vapor-liquid equilibrium data. For one, pressure sensors in the lab could be sampled closer to the time that the New Castle County Airport reports the barometric pressure to achieve a better correction for the pressure measured in the lab. While properly calibrating the thermocouples prior to performing the experiment would obtain more accurate temperature measurements. This is time consuming, so perhaps only a few thermocouples should be calibrated and the rest of them could record in reference to the calibrated devices. Finally, the fifth and sixth apparatuses or "units" could be used to measure the final binary system, instead of the vapor pressure, so that experimental values are available for all infinite dilution activity coefficients to regress ternary behavior.

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Appendix A - Low Pressure Justification

The low pressure assumption can be justified for this system through calculating the maximum error that would be expected in neglecting both the ratio of the fugacity coefficients and the Poynting pressure correction. These errors would be maximized at the maximum pressure that the binary solution is expected to achieve. Using Aspen plus to obtain predicted binary system behavior using the UNIFAC predictive model this maximum pressure can be estimated as for 2.15 bar for methanol and methyl acetate and 1.95 bar for acetone. Using these pressures and the physical properties provided in Table 1, the fugacity coefficient can be obtained at saturation and at the maximum pressure at 75 ℃ using supplemental equation (1) below.

$$\ln(\phi) = (Z^V - 1) - \ln(Z^V - B) - \frac{A}{2\sqrt{2}B} \ln \left(\frac{Z^V + (1 + \sqrt{2})B}{Z^V + (1 - \sqrt{2})B} \right)$$

(1)

Supplemental equation (1) gives the fugacity coefficient for a substance using the Peng-Robison equation of state, where Z^V is the compressibility of the vapor phase and A and B are constants in the equation of state. Carrying out these calculations gives values present in Supplemental Table 1. From this, one can see that the assumption of the ratio of the fugacity coefficients is one at most imparts 1.066% error into the calculation in the case of methanol, which is reasonable given other errors associated in the measurement.

Supplemental Table 1: Calculation of error due to neglecting the ratio of the fugacity coefficients

compound	ϕ, sat	ϕ, max P	ratio	Error (%)
methanol	0.975	0.965	0.989	1.066
acetone	0.955	0.953	0.997	0.259
methyl acetate	0.955	0.9474	0.992	0.796

A similar analysis can be completed using these maximum pressures to determine the maximum error imparted by neglecting the Poynting pressure correction. This was done by calculating this correction given in supplemental equation (2), where $\underline{V}_i^L$ is the liquid molar volumes calculated using the Peng-Robison equation of state

$$Correction = \exp \left(\frac{\underline{V}_i^L [P_{total} - P_i^{vap}(T)]}{RT} \right)$$

(2)

This was completed in Supplemental Table 2 below, which again indicated that the largest error would be only 0.11% for methanol, which is small enough to make neglecting this correction justifiable.

Supplemental Table 2: Calculation of Error due to neglecting the Poynting Correction

compound	$\underline{V}$ (m^3/mol)	Correction	Error (%)
methanol	5.06E-05	1.0011	0.1124
acetone	8.81E-05	1.0003	0.0295
methyl acetate	9.00E-05	1.0010	0.0997

Therefore, due to the small relative error (less than 0.11%) that is introduced by making these low pressure assumptions, equation (3) is a valid approximation of equation (2).

Appendix B - Safety Hazards and Handling of Chemicals

<u>Acetone</u>

Acetone is an extremely flammable and volatile organic compound as with the other chemicals used in this lab. The flash point of acetone is around -20℃ which was taken into consideration when performing the experiment. The group was careful to keep any sources of ignition away from the chemical at all times as it decomposes into CO and CO_2. The inhalation of acetone can cause acute dizziness and drowsiness. Prolonged exposure can cause issues in the respiratory system. With the small amount of acetone involved in this lab, the risks of inhalation of the chemical are extremely small, however, extra care was taken to keep the chemical away from the face and closed at all times at which it is not being used. If acetone is to get into contact with the skin it can cause irritations and inflammation. The risk of skin exposure was minimized by wearing the proper PPE.

<u>Methanol</u>

Methanol is another flammable organic used in this experiment and was kept away from any sources of ignition throughout the duration of the lab. The volatility of methanol is not as big a concern with a flash point of 12℃, however the inhalation of methanol can cause terrible symptoms. Methanol is toxic and the inhalation of it can result in CNS depression with nausea, headache, vomiting, dizziness and incoordination. In high amounts it can result in blindness and even death. These are serious concerns to take into consideration, however again the amount of methanol used in this experiment is not close to intolerable levels of the chemical. Exposure to someone's skin results in mild irritation at the place of contact. Chronic exposure to one's skin can cause defatting of the skin and dermatitis. The proper personal protective equipment worn in the lab was able to keep this risk at a minimum.

<u>Methyl Acetate</u>

Methyl acetate is another flammable and volatile organic compound with a flash point of -12℃. Proper precaution was exercised to keep the chemical away from any open flames to avoid igniting the vapor. The solvent was also kept capped to ensure it does not evaporate. Inhalation of the chemical can cause minor respiratory irritations so the chemical should remain capped and away from the mouth and nose at all times. Exposure to skin can cause mild irritation, skin cracking and drying.

Appendix C - Calibration of Measurement Devices

Calibration of pressure measurements

The accuracy of the pressure readings from each unit evaluated by comparing the value recorded prior to sealing the unit to the barometric pressure measured at the New Castle County Airport. As the cells were sealed between 12:17-12:31, while these barometric pressure readings are made on the 51st minute of every hour, the barometric pressure was plotted over time to try to estimate the pressure at each specific seal time. This is presented in Supplemental Figure J.
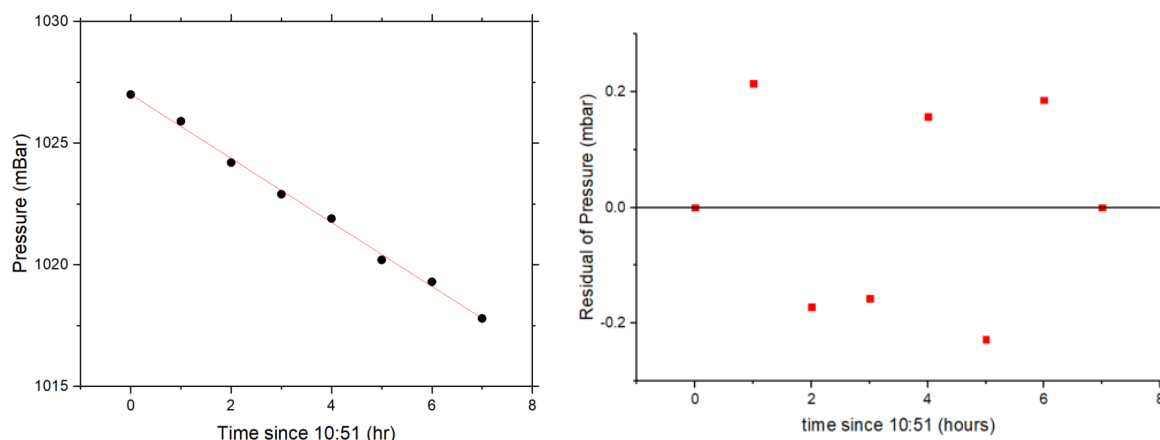
Supplemental Figure 1: Barometric pressure over time since 10:51 (left) and residuals of best fit line (right).

As the plot in Supplemental Figure 1 is rather linear, a linear least squares fit was completed, the residuals of which were normally distributed around ± 0.2 mbar indicating decent fit. This fit equation is given in equation (J) below, where P is in mbar and t is in hours since 10:51.

$$P = 1027.0 \pm 0.1 - (1.31 \pm 0.03) \times t \tag{J}$$

Using this equation, the approximate barometric pressure can be calculated at each time the cell was sealed. Through propagating the uncertainty in this expression, the uncertainty in this approximate barometric pressure over the time range of interest is approximately ± 0.3 mbar. As the experiment occurred in the basement of Colburn, by assuming that this is about six meters below the airport, with an average air density of 1.225 kg/m^3, a correction of 24 Pa can be subtracted from the difference in the measured pressure and the barometric pressure. The results of this calculation are given in Supplemental Table 3.

Supplemental Table 3: Comparison of barometric pressure to pressure before sealing the units

Unit #	unit pressure (mbar)	approx barometric pressure (mbar)	unit P - barometric P - height correction (mbar)	% Deviation from barometric pressure
1	1025.22(1)	1025.1(3)	-0.2(3)	-0.01(3)
2	1025.13(1)	1025.1(3)	-0.2(3)	-0.02(3)
3	1025.04(1)	1025.0(3)	-0.2(3)	-0.02(3)
4	1024.97(1)	1024.9(3)	-0.2(3)	-0.02(3)
5	1024.87(1)	1024.9(3)	-0.2(3)	-0.02(3)
6	1024.80(1)	1024.8(3)	-0.3(3)	-0.03(3)

From supplemental Table 3, one can see that the pressures recorded by the airport, when approximated to the times of interest, match those recorded by the pressure sensor in lab, when taking the uncertainties in each measurement into account. This is due to the relatively large uncertainty in the actual barometric pressure at the time of sealing the cell. When the additional pressure contribution of being below ground is added there is an approximate -0.02 ± 0.3 % deviation from barometric pressure, which is reasonable considering that the lab would operate at a low negative pressure. As the exact specifications of the negative pressure with which this lab operates under are not known, that the error in the difference between the pressure measurements is greater than the deviation itself, and that the values given are reasonable, these pressure sensors will be taken as well calibrated. A better calibration could have been obtained by knowing the expected offset between Colburn lab and the barometric pressure at the exact time of interest.

Calibration of Temperature Measurements
To accurately calibrate the K-type thermocouples used in the apparatuses, the ambient temperature reading of all thermocouples was measured prior to starting the lab. An estimation for the average deviation in each thermocouple reading was then made by comparing their ambient temperature reading to an estimation of the room temperature.

The room temperature was estimated by first determining the actual temperature that corresponds to the measured pressure of pure acetone, prior to the addition of any solute, in unit three. This was completed by rearranging the Antoine equation to solve for temperature using NIST parameters. This temperature was taken to be the actual temperature of the unit when it equilibrated with pure acetone, so that an offset in the temperature between that recorded and these values can be determined for each thermocouple. This offset was then assumed to be constant for the full temperature range, such that it could be used to determine the room

temperature by applying it to the ambient temperature readings. Using this strategy, the room temperature was determined to be 24.73 ± 0.03℃.

The pure acetone sample was chosen as, indicated in Table 1, it has the highest purity, indicating that its vapor pressure at any temperature should most closely match that of the NIST parameters. To check this value, the same treatment was also carried out for methanol, which had the next highest purity, using the pure solvent values at a nominal 75 ℃ for unit 1 and 5. This found an almost identical room temperature of 24.73 ± 0.06 ℃. Therefore, by using 24.73 ℃ as an estimate for the room temperature, the deviation in temperature for each thermocouple can be determined by comparing it to this value. This deviation, assuming that it is constant over this relatively small temperature range, can then be extrapolated to all subsequent temperature readings, correcting them. These deviations are given in Supplemental Table 4 below. This will act as the calibration of the thermocouples.

Supplemental table 4: Temperature difference between actual ambient temperature deduced by acetone and methanol vapor pressure correlations and the temperature recorded at ambient conditions for all thermocouples in all units.

Unit	TC1 ΔT (℃)	TC2 ΔT (℃)	TC3 ΔT (℃)	TC4 ΔT (℃)	TC5 ΔT (℃)	TC6 ΔT (℃)
1	-0.03	0.01	-0.07	-0.2	-0.2	-0.06
2	-0.18	0.03	-0.1	-0.16	0.02	-0.06
3	-0.12	-0.19	-0.21	-0.13	-0.13	0.06
4	0.01	-0.07	-0.08	-0.01	-0.07	-0.15
5	0.02	0.03	-0.07	-0.2	-0.18	-0.06
6	-0.07	-0.06	-0.01	-0.15	-0.01	-0.01

Note that after making this correction, the temperatures recorded by the various thermocouples during the experiments were rather consistent (average standard deviation of 0.04 for all points), indicating that the assumption of a constant offset temperature was accurate. This allows for accurate averaging of these values, to reflect the temperature of the apparatus at each equilibrium sampling point.

Appendix D - Experimental Data

Supplemental Figure 2 below gives the equilibrium absolute pressure of each unit plotted over time. As is evident in this figure, there are no major deviations. Although The third point in each injection may seem somewhat out of place, as it breaks the general linear trend, it is most likely the case that slightly less time was given for the prior injection to equilibrate, shifting the presence of this point slightly towards the left. This makes it seem out of place, however, the pressure increase seems realistic.
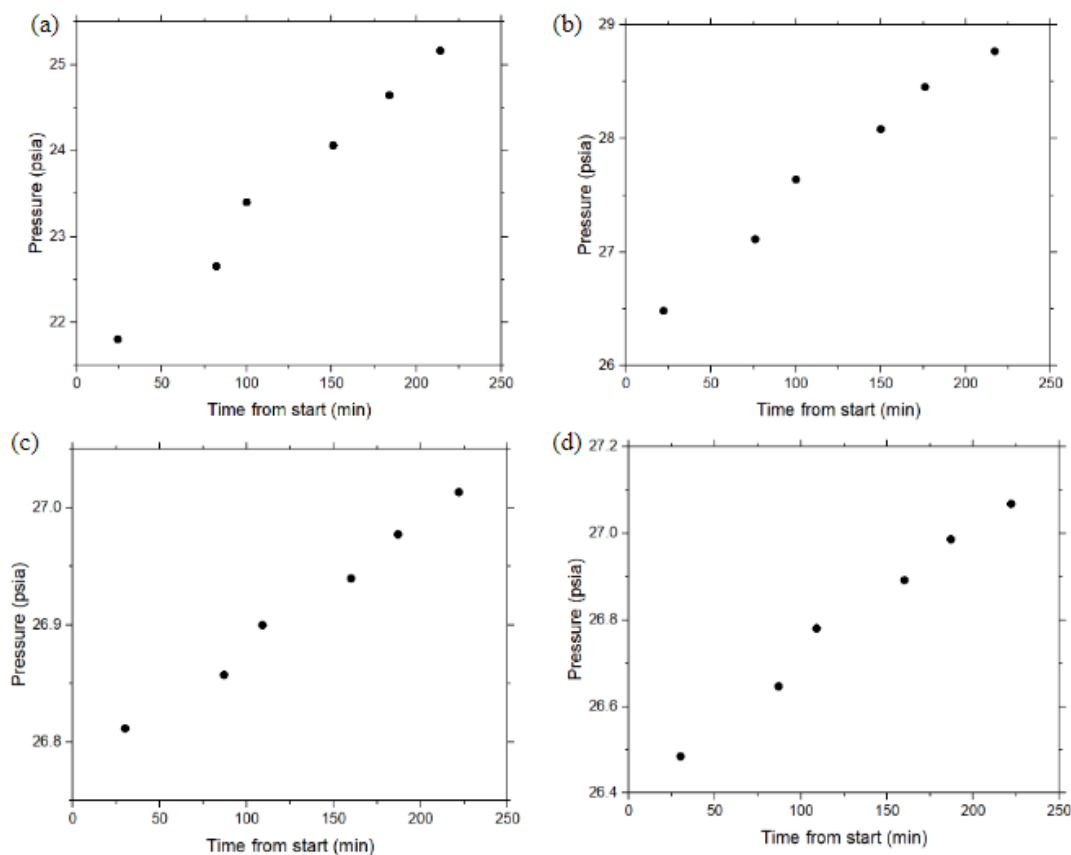
Supplemental Figure 2: Pressure over time from start of experiment for (a) methyl acetate in methanol, (b) methanol in methyl acetate, (c) methyl acetate in acetone, and (d) acetone in methyl acetate.

The measured temperatures and pressures are recorded for each unit below after the system equilibrated in Supplemental Tables 5-10. The errors in the mole fraction, average temperature, and pressure are recorded as plus or minus the least significant digit as the value in the parenthesis. The values for the mole fraction were calculated using the density of the solutes and solvents. The temperatures recorded are the average of the corrected temperatures of each thermocouple. Appendix D covers how these corrections were calculated.

Supplemental Table 5: VLE data for MeOAc in MeOH, completed in unit 1.

Injection #	Mole Fraction MeOAc	Ave corrected temp (°C)	Pressure (psia)
0	0	74.92(5)	21.8062(3)
1	0.02622(3)	74.92(5)	22.6551(3)
2	0.05110(4)	74.91(5)	23.4008(3)
3	0.07474(5)	74.92(5)	24.0594(3)
4	0.09723(6)	74.92(5)	24.6433(3)
5	0.11865(7)	74.93(5)	25.1619(3)

Supplemental Table 6: VLE data for MeOH in MeOAc, completed in unit 2.

Injection #	Mole Fraction MeOH	Ave corrected temp (°C)	Pressure (psia)
0	0	74.92(5)	26.4846(3)
1	0.0232(1)	74.92(5)	27.1146(3)
2	0.0455(1)	74.94(5)	27.6397(3)
3	0.0666(2)	74.92(5)	28.0813(3)
4	0.0868(2)	74.91(5)	28.4522(3)
5	0.1062(2)	74.92(5)	28.7670(3)

Supplemental Table 7: VLE data for MeOAc in DMK, completed in unit 3.

Injection #	Mole Fraction MeOAc	Ave corrected temp (°C)	Pressure (psia)
0	0	74.92(5)	26.8117(3)
1	0.02001(6)	74.92(5)	26.8574(3)
2	0.03923(8)	74.92(5)	26.8999(3)
3	0.0577(1)	74.91(5)	26.9397(3)
4	0.0755(1)	74.90(5)	26.9773(3)
5	0.0926(1)	74.91(5)	27.0134(3)

Supplemental Table 8: VLE data for DMK in MeOAc, completed in unit 4.

| Injection #	Mole Fraction DMK	Ave corrected temp (°C)	Pressure (psia)
0	0	74.90(5)	26.4844(3)
1	0.02226(7)	74.91(5)	26.6462(3)
2	0.04355(9)	74.89(5)	26.7800(3)
3	0.0639(1)	74.90(5)	26.8912(3)
4	0.0835(1)	74.90(5)	26.9856(3)
5	0.1022(1)	74.89(5)	27.0673(3)

Supplemental Table 9: Vapor Pressure Measurements for MeOH, completed in unit 5.

| Nominal Temp (℃)	Ave corrected temp (°C)	Pressure (psia)
25	24.92(5)	2.4461(2)
30	29.92(5)	3.1579(2)
35	34.92(5)	4.0387(2)
40	39.93(5)	5.1194(2)
45	44.93(5)	6.4358(2)
50	49.92(5)	8.0275(2)
55	54.94(5)	9.9371(2)
60	59.93(5)	12.2145(2)
65	64.92(5)	14.9119(2)
70	69.75(5)	18.0876(2)
75	74.93(5)	21.8058(2)
80	79.93(5)	26.1354(2)
85	84.91(5)	31.1503(2)
90	89.92(5)	36.9298(2)

Supplemental Table 10: Vapor Pressure Measurements for MeOAc, completed in unit 6.

Nominal Temp (℃)	Ave corrected temp (°C)	Pressure (psi)
25	24.94(5)	4.1658(2)
30	29.93(5)	5.1821(2)
35	34.91(5)	6.3906(2)
40	39.93(5)	7.8183(2)
45	44.94(5)	9.4917(2)
50	49.94(5)	11.4418(2)
55	54.94(5)	13.6991(2)
60	59.92(5)	16.2964(2)
65	64.92(5)	19.2692(2)
70	69.91(5)	22.6527(2)
75	74.93(5)	26.4841(2)
80	79.93(5)	30.8054(2)
85	84.77(5)	35.6515(2)
90	89.93(5)	41.0683(2)

Appendix E - Residuals Analysis of Regressed Fits
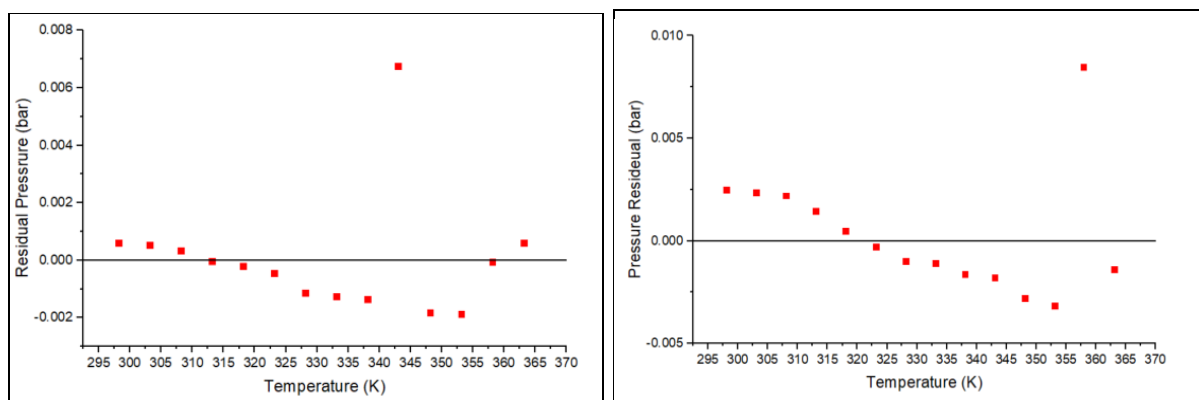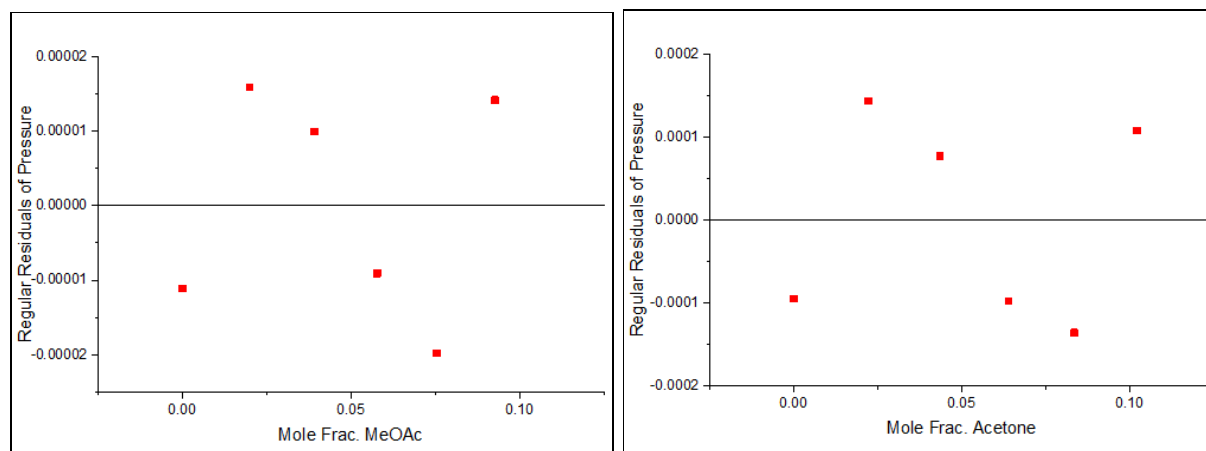

Supplemental Figure 2: Residuals for Figure 1, residuals of the antoine fit of vapor pressure for methyl acetate (left) and methanol (right).
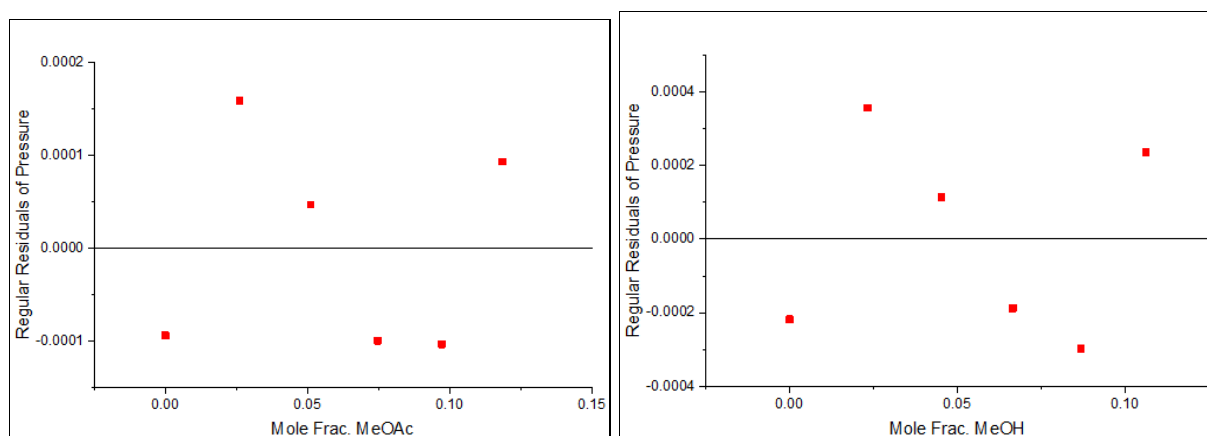
Supplemental Figure 3: Residuals for Figure 5, residuals of the quadratic fit of pressure (left) over mole fraction of methyl acetate in methanol and (right) over mole fraction of methanol in methyl acetate

Residuals for MeOAc-Acetone near the limit of infinite Dilution for MeOAc

Supplemental Figure 4: Residuals for Figure 5, residuals of the quadratic fit of pressure (left) over mole fraction of methyl acetate in acetone and (right) over mole fraction of acetone in methyl acetate.

Appendix F - Additional Equations/ Sample Calculations

1. Infinite Dilution Activity Coefficient for MeOAc in Acetone

$$\gamma_1^\infty = \frac{P_2^{vap}(T) + \left(\frac{\partial P_{tot}}{\partial x_1}\right)_{x_1 \rightarrow)}}{P_1^{vap}(T)} = \frac{1.8531 + 0.15785}{1.8287} = 1.0997$$

2. Vapor Pressure Calculation for MeOAc

$$P_{vap}(T) = 10^{\left(A - \frac{B}{T+C}\right)} = 10^{4.21 - \frac{1170}{348.15 - 52}} = 1.8287$$

3. Addition/Subtraction Error Propagation

$$y \pm \sigma_y = (x \pm \sigma_x) + (z \pm \sigma_z) = (2 \pm 0.07) + (6 \pm 0.12) = 8 \pm 0.14$$

$$\sigma_y = \sqrt{\sigma_x^2 + \sigma_z^2} = \sqrt{(0.07)^2 + (0.12)^2} = 0.1389$$

4. Division/Multiplication Error Propagation

$$y = \frac{x}{z}; or \; y = xz$$

$$\sigma_y = |y|\sqrt{\left(\frac{\sigma_x}{x}\right)^2 + \left(\frac{\sigma_z}{z}\right)^2} = 12\sqrt{\left(\frac{0.07}{2}\right)^2 + \left(\frac{0.12}{6}\right)^2} = 0.4837$$

5. Logarithm Function Error Propagation (Used in Antoine parameter regression)

$$P_{vap}(T) = 10^x$$

$$\sigma_{Pvap} = 2.303 * P_{vap}(T) * \sigma_x = 2.303 * (1.8287) * 0.0116 = 0.049$$

6. Purity correction for methyl acetate in methanol, assuming the impurities are water

   11.817 g solvent with 2.2256 g solute

$moles\ MeOH\ =\ 0.999 \times (mass\ solvent)/MW_{MeOH} = 0.999 \times (11.817g)/(32.04\ g/mol)\ =\ 0.3685$

$moles\ water\ (solvent)\ =\ 0.001 \times (11.817g)/(18.015g/mol)\ =\ 0.0006559$

$moles\ MeOAc\ =\ 0.998 \times (mass\ solute)\ /\ MW_{MeOAc} = 0.998 \times (2.2256g)/(79.08g/mol)\ =\ 0.02809$

$moles\ water\ (solute)\ =\ 0.002 \times (2.2256\ g)/(18.015\ g/mol)\ =\ 0.0002471$

$x_{MeOAc}\ =\ mole\ MeOAc/(mole\ MeOH\ +\ mole\ water\ (solvent\ and\ solute))$

$x_{MeOAc}\ =\ 0.02809\ /\ (0.3685\ +\ 0.0006559\ +\ 0.0002471\ +\ 0.02809) = 0.07067$