CHAPTER

SIX

THERMODYNAMICS

6.1. Vapor-Liquid Equilibrium in a Binary System
6.2. Investigation of the Thermodynamic Properties of Pure Water
6.3. Estimating Vapor-Liquid Equilibrium Parameters via a Rotary Evaporation Process

6.1. VAPOR-LIQUID EQUILIBRIUM IN A BINARY SYSTEM

Keywords: *Thermodynamics, vapor-liquid equilibrium (VLE), non-ideal solution, azeotrope.*
Before the experiment: *Read the booklet carefully. Be aware of the safety precautions.*

6.1.1. Aim

To investigate vapor-liquid equilibrium (VLE) behavior of the azeotrope forming binary system of acetone-chloroform, to determine the experimental activity coefficients and to verify these values through data reduction method and Margules equations.

6.1.2. Theory

6.1.2.1. Vapor/Liquid Equilibrium and Phase Rule

Vapor/liquid equilibrium (VLE) designates a static condition where no change occurs in the macroscopic properties of a system with time. If enough time passes for an isolated system, where liquid and vapor phases are in contact, eventually the mixture will reach an equilibrium state. At microscopic level conditions of individual molecules are not static and molecules with enough energy can pass into the other phase but at equilibrium, the net transfer of material between phases is zero. In engineering applications, equilibrium state is never reached but assumed to be reached with a satisfactory accuracy. In a boiling liquid mixture, compositions of liquid and vapor phases change with time; however if the vaporization rate is small, then the mixture can be assumed to be at equilibrium. Based on this assumption, VLE parameters can be predicted experimentally [1].

For a non-reacting system, the number of variables that may be independently fixed in a system at equilibrium can be calculated according to the phase rule [1]:

$$F = 2 - \pi + N \tag{6.1.1}$$

where F is a degree of freedom, π is the number of phases and N is the number of species present. Phase rule suggests that if number of species and phases in a system are known, a certain system can be defined with F different intensive properties.

6.1.2.2. Modeling of VLE and Activity Coefficient

Modeling of VLE behaviour of solutions can be done with different sets of assumptions based on temperature, pressure and the chemical properties of the species forming the solution. The simplest model, Raoult's Law, assumes both vapor and liquid phases are ideal. It is formulated as [1]:

$$y_i P = x_i P_i^{sat} \tag{6.1.2}$$

where P is the pressure; y_i, x_i, and P_i^{sat} are the vapor mole fraction, liquid mole fraction and saturation pressure of the i^{th} species, respectively. Raoult's Law works well at low to moderate pressures for mixtures comprising of chemically similar species. For chemically different species at low to moderate pressures, results of Raoult's Law begin to deviate from experimental data. A modified version of the Raoult's Law, considering the vapor phase as ideal but the liquid phase as real, gives more realistic results [1]. It can be written as:

$$y_i P = x_i \gamma_i P_i^{sat} \tag{6.1.3}$$

where γ_i is the activity coefficient for the i^{th} species, and it represents the non-idealities in the liquid phase. If the compositions of vapor and liquid phases are known, then activity coefficients at different equilibrium conditions for each species can be calculated.

6.1.2.3. Calculating Activity Coefficient from Data Reduction Method

Non-idealities in liquid phase are related with excess Gibbs energy. The relation between activity coefficients and excess Gibbs energy is given as [1]:

$$\overline{G}_i^E = RT\ln\gamma_i \tag{6.1.4}$$

where $\overline{G}_i^E$ is the partial molar excess Gibbs energy of i^{th} species. $\ln\gamma_i$ is a partial property with respect to G^E/RT; hence for a binary mixture excess Gibbs energy can be written as:

$$\frac{G^E}{RT} = x_1\ln\gamma_1 + x_2\ln\gamma_2 \tag{6.1.5}$$

Eq. 6.1.5 enables calculation of excess Gibbs energy for a mixture if VLE data is already available or obtained from an experiment. Margules Gibbs Energy Model, founded by Max Margules in 1895, is a simple thermodynamic model about Gibbs free energies of liquids in mixture [1]. In chemical engineering practice, this is known as Margules Activity Model. Excess Gibbs energy of a binary system is given by Margules as following:

$$\frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2)x_1x_2 \tag{6.1.6}$$

where A_{21} and A_{12} are the Margules parameters for a binary mixture. Eq. 6.1.6 can be written as:

$$\frac{G^E}{RTx_1x_2} = A_{21}x_1 + A_{12}x_2 \tag{6.1.7}$$

The nature of Eq. 6.1.7 suggests using a straight line for approximating $\frac{G^E}{RTx_1x_2}$ behavior. If experimental $\frac{G^E}{RTx_1x_2}$ data versus x_1 (or x_2) is plotted, the intercepts of the line with the y-axis would give Margules parameters A_{21} and A_{12} as in Figure 6.1.1:

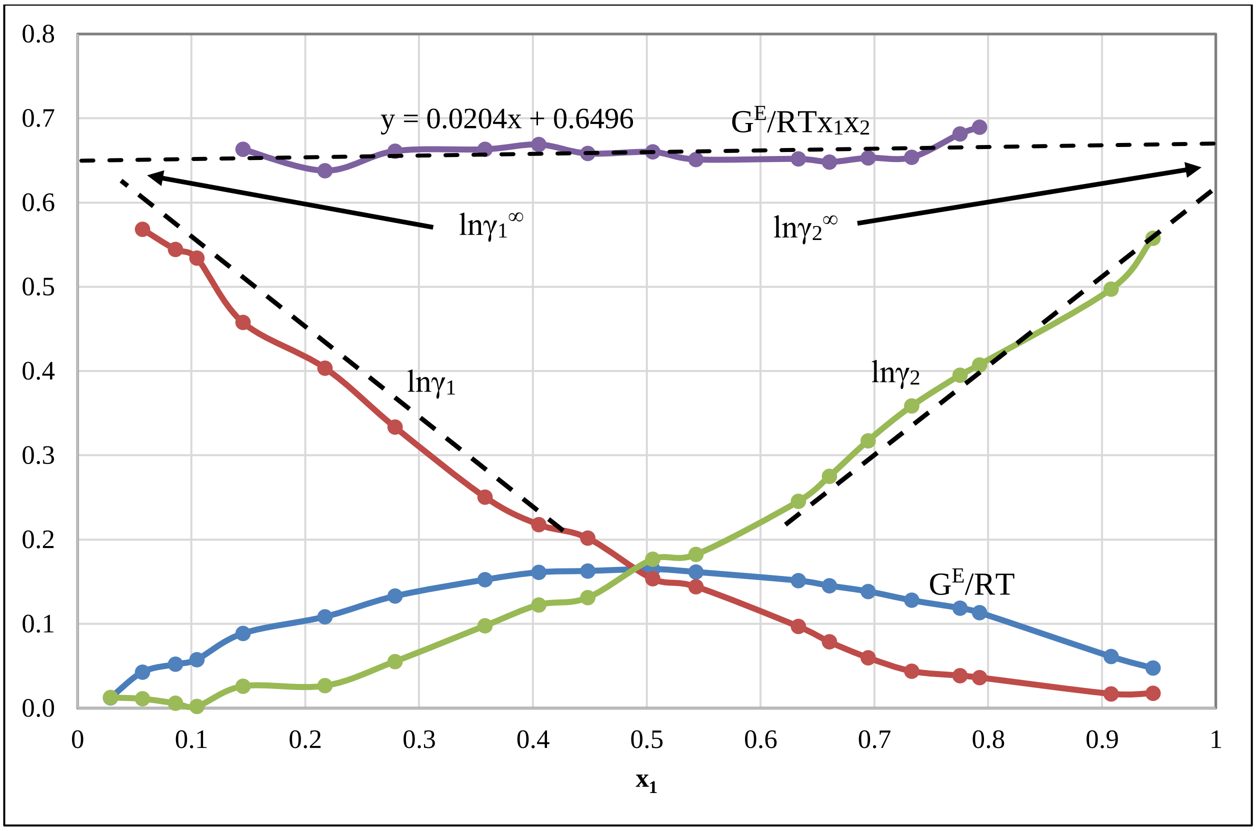

Figure 6.1.1. Liquid-phase properties and their correlations.

When the Margules parameters are obtained, activity coefficients for a binary mixture can be calculated, when Eq. 6.1.5 and Eq. 6.1.6 are combined:

$$\ln\gamma_1 = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1] \quad (6.1.8)$$

$$\ln\gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2] \quad (6.1.9)$$

These are the Margules equations, and they represent a commonly used empirical model of solution behavior. For the limiting conditions of infinite dilution, they become:

$$\ln\gamma_1{}^{\infty} = A_{12} \quad (x_1 = 0) \quad (6.1.10)$$

$$\ln\gamma_2{}^{\infty} = A_{21} \quad (x_2 = 0) \quad (6.1.11)$$

6.1.2.4. Azeotrope Formation in a Binary Mixture

More than often, mixtures consisting of at least two components form an azeotrope, which occurs when liquid and vapor fractions cannot be changed during distillation [2]. An azeotrope can result in two conditions, where the mixture can boil at either higher or lower temperature than the boiling points of any species forming the mixture. Figure 6.1.2 (a) shows temperature vs. composition diagram of non-azeotrope forming mixture. Figures 6.1.2 (b) and 6.1.2 (c) show temperature vs. composition diagrams of maximum-boiling and minimum-boiling azeotrope forming mixtures, respectively.

In ideal solutions, properties of a mixture are directly related with those of the pure components in the mixture. If a mixture is composed of chemically similar molecular structure, VLE behavior of such mixtures can be expressed by the famous Raoult's law. Azeotropes do not conform to this idea; during boiling, the composition of the liquid phase is equal to that of the vapor phase [2].

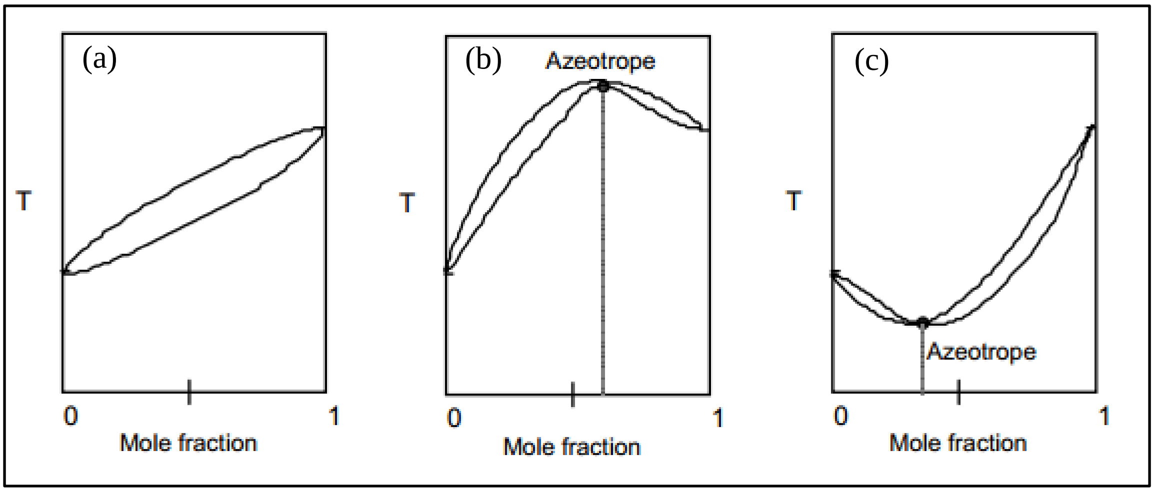

Figure 6.1.2. Composition vs. temperature diagram of binary system [3].

6.1.3. Experimental Setup

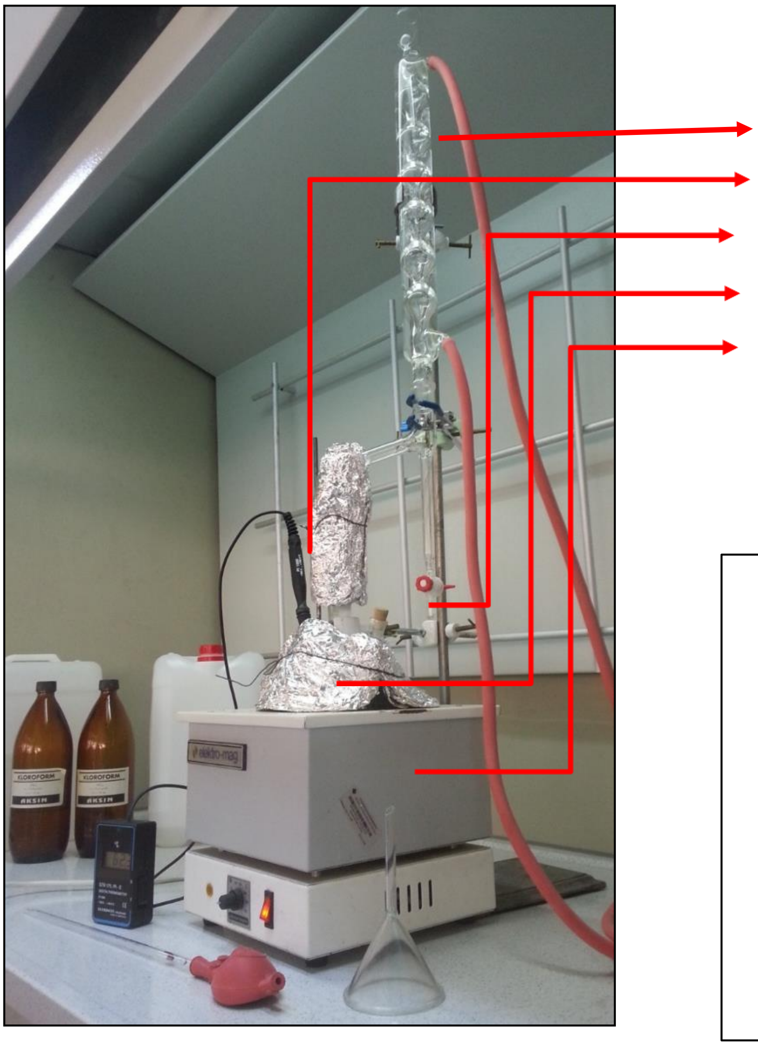

Figure 6.1.3. Experimental setup.

Figure 6.1.4. Abbe refractometer [4].

6.1.4. Procedure

1. Prepare the experimental setup as shown in Figure 6.1.3 and fill the flask with 100 ml of pure acetone.
2. Provide insulation around the flask to decrease heat loss. Put a few boiling chips inside the flask.
3. Turn on the heater and wait for the temperature inside the flask to stabilize.
4. After distillate starts to accumulate in the distillate reservoir (A from Figure 6.1.3) collect a sample. Collect another sample from the flask (B from Figure 6.1.3). Record the temperature inside the flask.
5. Turn off the heater and analyze both samples via refractometer.
6. Add 50 ml of chloroform to the solution in the flask successively for 6 times. After each addition repeat steps 3-5.
7. At the end of the experiment, be sure that all used chemicals are collected into the waste disposal container.

Safety Issues: In this experiment acetone and chloroform will be used as chemicals. Due to their hazardous and corrosive nature, avoid skin and eye contact while handling chemicals. Avoid wearing contact lenses. The experiment will be performed under a hood. Do not inhale any chemical vapors. In case of any skin or eye contact with chemicals, wash contacted area with plenty of water, and report it to your TA. For further information, check MSDS of acetone and chloroform [5, 6]. Beware of heater. Apparatus is made of glass and requires gentle handling. Make sure to turn off the cooling water at the end of the experiment.

6.1.5. Report Objectives

1. For 7 different overall compositions, convert refractive indices of samples collected from distillate and flask to mole fractions.
2. Plot temperature vs. liquid-vapor fraction (T-x-y) graph.
3. Calculate partial pressures of acetone and chloroform using Antoine equation, then calculate activity coefficients using Modified Raoult’s law for each equilibrium point. Use these values to calculate G^E/RTx_1x_2 for all equilibrium points.
4. Find Margules equation parameters using graphical data reduction method.
5. Calculate the activity coefficients for your experimental VLE data, using the calculated Margules parameters and compare them with the ones calculated in 3rd objective.

6. State the azeotrope conditions for acetone-chloroform binary mixture according to experiment and compare your results with the ones in literature.

References

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6. Chloroform Material Safety Data Sheet, http://www.sciencelab.com/msds.php?msdsId=9927133 (Last update May 2013. Retrieved February 2015).
7. Vapor Liquid Equilibrium Data of Acetone and Chloroform,
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   (Retrieved February 2015).

Appendix

Table A.1. Mole fractions vs refractive indices for acetone-chloroform mixture.

Acetone (mol fraction)	**n_D**
0	1.4461
0.1	1.439
0.2	1.4301
0.3	1.4219
0.4	1.4148
0.5	1.4049
0.6	1.3941
0.7	1.3878
0.8	1.3772
0.9	1.3671
1	1.3589

Table A.2. VLE data for acetone/chloroform mixture [7].

T (K)	**$x_{acetone}$**	**$y_{acetone}$**
335.75	0.098	0.060
336.65	0.186	0.143
337.25	0.266	0.230
337.55	0.360	0.360
336.95	0.468	0.514
335.85	0.578	0.646
334.65	0.673	0.751
333.45	0.755	0.830
332.15	0.827	0.890
331.05	0.892	0.939
330.15	0.949	0.975

6.2. INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF PURE WATER

Keywords: *Thermodynamics, enthalpy and entropy of vaporization, boiling temperature.*

Before the experiment: *Read the booklet carefully. Be aware of the safety precautions. No chemicals are required. Make sure to unplug the water bath after completing the experiment.*

6.2.1. Aim

The main purpose of this experiment is to investigate the thermodynamic properties, which are enthalpy of vaporization, entropy of vaporization and boiling temperature, for pure water by deducing the vapor pressure of pure water as a function of temperature via Clausius-Clapeyron relation.

6.2.2. Theory

The vapor pressure of a liquid is the equilibrium pressure of a vapor above its liquid that is resulted from evaporation of a liquid above a sample of the same liquid in a closed container [1]. Liquids and some solids are continuously vaporizing, meaning that atoms or molecules in the liquid or solid are moving into the gas phase. Molecules will leave the liquid if they have enough energy and some of these molecules will return to the liquid after losing their energies in collisions. If the container is closed, the molecules cannot escape and equilibrium is reached when the rate of molecules leaving the liquid equals the rate of molecules returning to the liquid. The number of molecules in the gas phase does not change at equilibrium and the pressure that they exert is called the vapor pressure of liquid [2].

Vapor pressure of liquids depends on the temperature and the nature of the liquid. The forces causing the vaporization of a liquid are derived from the kinetic energy of translation of its molecules. An increase in kinetic energy of molecular translation increases the rate of vaporization and vapor pressure; hence fewer particles tend to condense. The nature (or structure) of the liquid is the other significant factor determining the magnitude of the equilibrium vapor pressure. Since all molecules are endowed with the same kinetic energies of translation at any specified temperature, the vapor pressure is entirely dependent on the magnitudes of the maximum potential energies of attraction which must be overcome in vaporization. These potential energies are determined by the intermolecular attractive forces. Thus, if a substance has high intermolecular attractive forces, the rate of loss of molecules from its surface becomes small and the corresponding equilibrium vapor pressure is low. The magnitudes of the attractive forces are dependent on both the size and structure of the molecules, usually increasing with increased size and structural complexity [3, 4].

Increase in the surface area of liquid does not affect the vapor pressure. If surface area of the liquid increases, this leads to a rise in the total rate of evaporation. However at the same time, condensation rate of vapor molecules increases at the same factor with the evaporation rate. Thus, vapor pressure does not alter with the change in the surface area of the liquid [3].

For a system consisting of vapor and liquid phases of a pure substance, this equilibrium state is directly related to the vapor pressure of the substance and vapor pressure changes nonlinearly with respect to temperature given by Clausius-Clapeyron relation [2]:

$$\frac{dlnP}{d(1/T)} = \frac{-\Delta H^{lv}}{R\Delta v} \tag{6.2.1}$$

Where P is the vapor pressure at a specific temperature T, ΔH^{lv} is the enthalpy of vaporization and Δv is the specific volume change of phase transition. By taking the integral of Eq. 6.2.1 after converting V terms to P and T, the linearized form Clausius-Clapeyron equation becomes:

$$\ln P_{vap} = \frac{-\Delta H_{vap}}{R}\frac{1}{T} + \frac{\Delta S_{vap}}{R} \tag{6.2.2}$$

Therefore, a plot of natural logarithm of the vapor pressure versus the reciprocal temperature gives a straight line. The slope of the line is equal to minus the enthalpy of vaporization divided by the universal gas constant, $-\Delta H_{vap}/R$, and the intercept is equal to the entropy of vaporization divided by universal gas constant, $\Delta S_{vap}/R$. The normal boiling temperature of pure species can be found as $\Delta H_{vap} / \Delta S_{vap}$ when P_{vap} is equal to the atmospheric pressure as 1 atm. In order to calculate the thermodynamic properties, pressure can be expressed as a function of temperature and molar volume using Equations of state (EOS), such as Redlich Kwong (RK), Peng Robinson (PR) and Van Der Waals. A useful auxiliary thermodynamic property is defined by the following equation:

$$Z = \frac{PV}{RT} \tag{6.2.3}$$

In the ideal state, it is assumed to have no molecular interactions leading to the compressibility factor (Z) as 1. However, to represent PVT behaviour of both liquid and vapor phases of a substance, EOS must encompass a wide range of temperatures and pressures. Polynomial equations that are cubic in molar volume offer a compromise between generality and simplicity that is suitable to many purposes. A general expression used for the calculation of air pressure is given as [1].

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)} \tag{6.2.4}$$

For a given equation, ϵ and σ are pure numbers, the same for all substances, whereas parameters $a(T)$ and b are substance dependent. The temperature dependence of $a(T)$ is specific for each equation of state and these parameters are calculated from the following equations:

$$a(T) = \Psi \frac{\alpha(T_r) R^2 T_c^2}{P_c} \tag{6.2.5}$$

$$b = \Omega \frac{RT_c}{P_c} \tag{6.2.6}$$

In these equations Ω and Ψ are pure numbers, independent of substance and determined for a particular equation of state from the values assigned to ϵ and σ. T_r is the reduced temperature which is the ratio of the temperature of the substance to its critical temperature T_c. In this experiment, the total pressure inside the cylinder, which is the sum of the vapor pressure of water and the trapped air, is equal to the atmospheric pressure and the air pressure in both ideal and real cases is attained using the equations mentioned before.

6.2.3. Experimental Setup

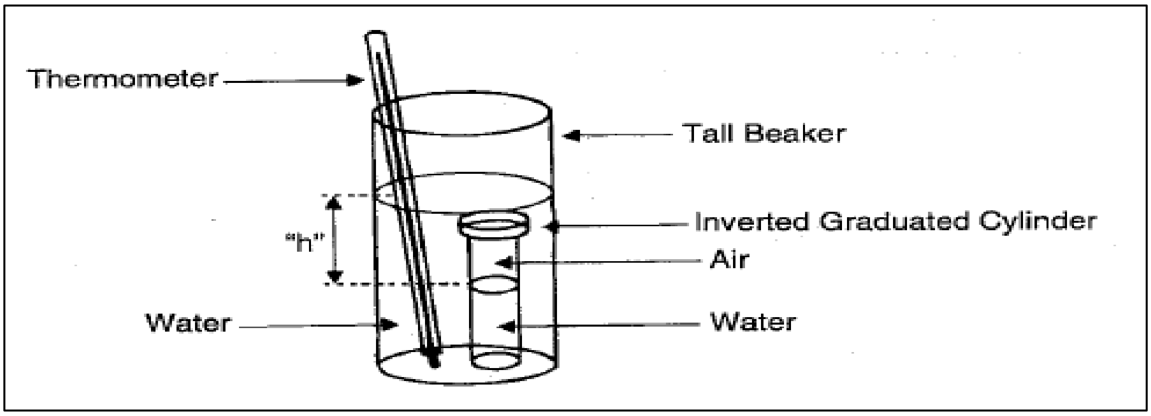

Figure 6.2.1. Schematic representation of the experimental setup.

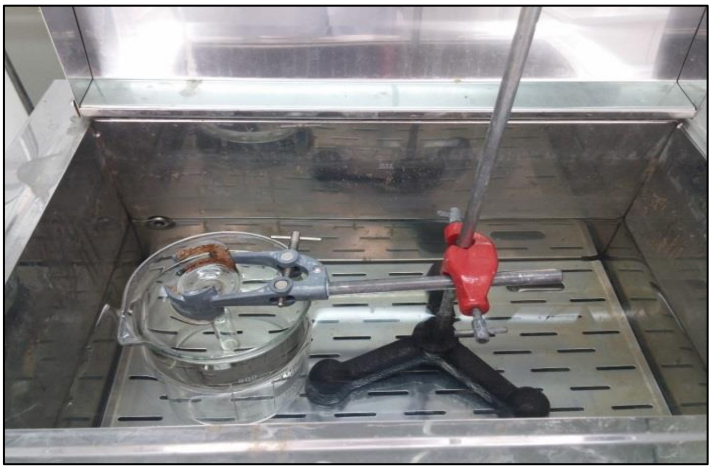

Figure 6.2.2. Experimental setup in water bath.

6.2.4. Procedure

1. A 1000 mL beaker is filled with distilled water until a nearly full level is reached.
2. A 10 mL graduated cylinder is filled with distilled water leaving a 2.5 cm length from the top, empty.
3. A finger is placed over the opening and then the graduated cylinder is rapidly inverted and placed into the beaker which is also filled with distilled water, as a result an air bubble is trapped at the top of the inverted cylinder.
4. The beaker is again filled with distilled water until the graduated cylinder is fully covered.
5. Thermocouple is replaced in the beaker.
6. The water is heated to 75 °C by using a water bath.
7. After reaching the desired temperature value, water bath is turned off.
8. At every 5 °C decrease in the temperature value, the corresponding air level in the cylinder is read and recorded.
9. When the temperature has dropped below 50 °C, the cooling process is performed by the addition of ice around the beaker and a temperature value below 10 °C is obtained.

6.2.5. Report Objectives

1. Plot ln P versus 1/T from experimental data.
2. Evaluate the thermodynamic properties for water and its boiling temperature.
3. Compare the results in ideal and real case where the theoretical values are calculated from two of the following cubic equations of state: van der Waals, Redlich-Kwong, Soave-Redlich-Kwong and Peng-Robinson (Note: Your TA will decide on which two to choose).

6.2.6. References

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6.3. ESTIMATING VAPOR-LIQUID EQUILIBRIUM PARAMETERS VIA A ROTARY EVAPORATION PROCESS

Keywords: *Thermodynamics, vapor/liquid equilibrium (VLE), non-ideal solution, Margules activity coefficient model, rotary evaporation, non-linear regression.*

Before the experiment: *Read the booklet carefully. Be aware of the safety precautions.*

6.3.1. Aim

To observe the vapour-liquid equilibrium (VLE) behavior of the acetone-water system with a Margules activity coefficient model, using a non-linear regression approach on the data gathered from the rotary evaporation process.

6.3.2. Theory

6.3.2.1. Vapor/Liquid Equilibrium

A closed and isolated system which comprises vapor coexisting with a liquid may be said to be at vapor/liquid equilibrium given there is no net flow of mass or energy between the phases. Practically, this implies that the phases must exist at the same temperature, pressure and chemical potential [1]. Although the rotary evaporation process does not take place in such a closed and isolated system, it may be assumed that the evaporation mixture is always in equilibrium if the evaporation is carried out gently enough.

The equality of chemical potential between the two phases is commonly described by models such as Raoult's Law, seen here [1]:

$$y_i \mathrm{P} = x_i P_i^{sat} \tag{6.3.1}$$

where y_i and x_i are the vapor phase and liquid phase mole fractions, respectively, of species i. P is the pressure in the environment, and P_i^{sat} is the saturation vapor pressure of species i.

Raoult's Law assumes an ideal vapor phase (the vapor phase is treated as an ideal gas) and an ideal liquid phase (the liquid phase behaves as if it were a pure liquid) [1]. However, water and acetone do not form an ideal solution because their dominant intermolecular forces are different. [2] To model this deviation from ideality, a modified version of Raoult's Law is used: [1]

$$y_i \mathrm{P} = x_i \gamma_i P_i^{sat} \tag{6.3.2}$$

Where γ_i is the activity coefficient associated with species i that describes this species' deviation from ideality when in the liquid phase with the other species in this mixture.

The P_i^{sat} values can be estimated using the Antoine equation, given temperature measurements, as below: [1]

$$\ln(P_i^{sat}) = A_i - \frac{B_i}{T+C_i} \tag{6.3.3}$$

6.3.2.2. Estimating Activity Coefficient Parameters

While a variety of models for the activity coefficient exist, in this experiment the Margules equations will be used due to their simplicity. For a two-component mixture, the Margules equations take this form: [1]

$$\ln\gamma_1 = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1] \tag{6.3.4}$$

$$\ln\gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2] \tag{6.3.5}$$

where A_{12} and A_{21} are adjustable parameters expressing the asymmetric behavior of the activity coefficents with respect to mixture composition.

Equation 6.3.2 can be written for both components and combined with Equations 6.3.4 and 6.3.5 to yield a relation between P and x_1, with A_{12} and A_{21} as adjustable parameters. These parameters can be determined by using a non-linear regression to P vs. x data.

6.3.2.3. Estimating Composition from Density

The density, ρ, of a mixture can be expressed as a function of the composition of the mixture. This function can be used to estimate mole fractions from simple mass and volume measurements.

$$\rho = m/V \tag{6.3.6}$$

However, due to the volume change of mixing, the volumes of the components are not additive [1]. An empirical "calibration curve" can be constructed by measuring the density of acetone-water mixtures prepared at known compositions. A linear or quadratic model can be fit to the data such as in the example below.

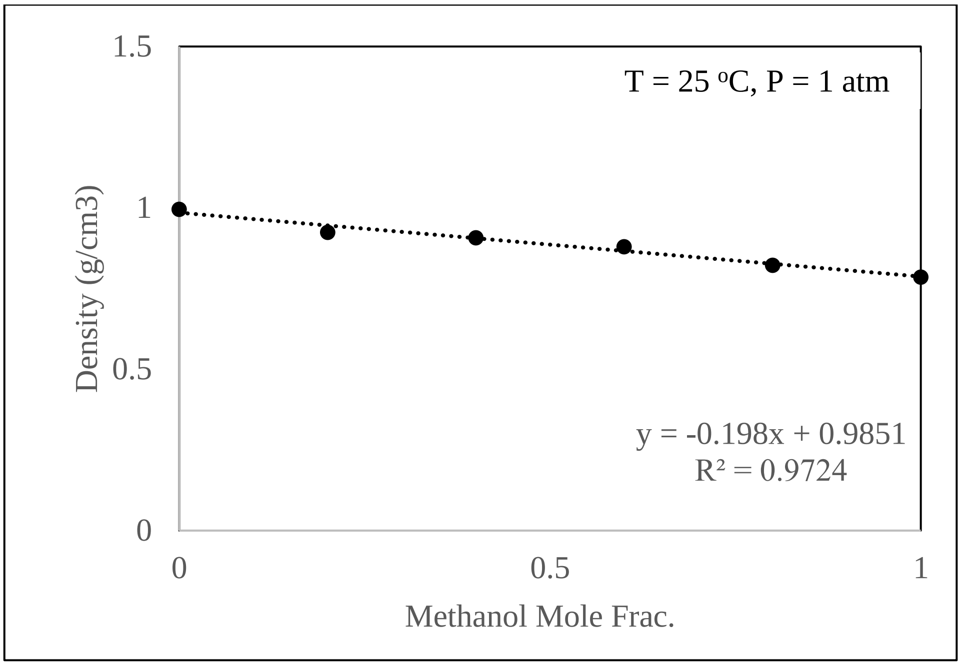

Figure 6.3. 1. Methanol-Water Density-Composition plot, adapted from Smith, Van Ness and Abbot [1].

6.3.3. Experimental Setup

The setup for this experiment is composed of the rotary evaporator assembly and the attached vacuum pump, shown below.

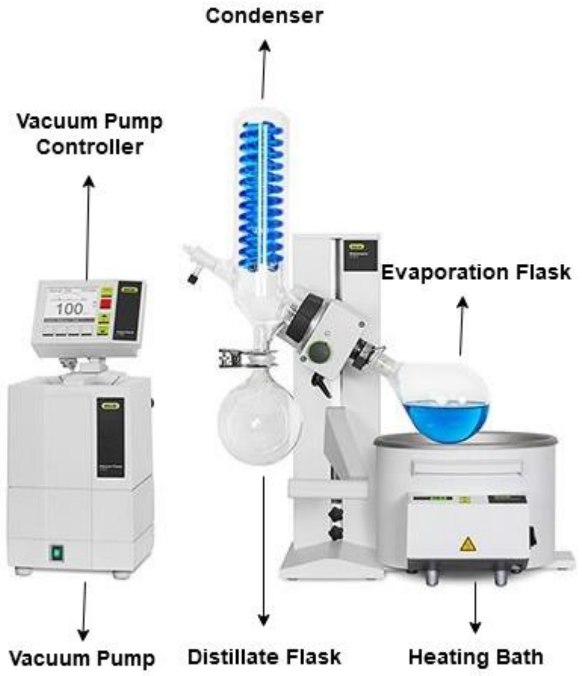

Figure 6.3. 2. The rotary evaporator setup [3].

6.3.4. Procedure

1. Clean a 100 mL graduated cylinder with acetone and distilled water. Record its weight.
2. Use two other graduated cylinders to measure precise volumes of the solvents water and acetone. Record the precise volumes of the two solvents. Combine them in the graduated cylinder weighed in step (1). Record the weight and volume of the solvent mixture. The following volumes of solvents are measured:
    - 20 mL acetone
    - 20 mL water
    - 75 mL acetone + 5 mL water
    - 70 mL acetone + 10 mL water
    - 60 mL acetone + 20 mL water
    - 40 mL acetone + 40 mL water
3. Make sure the heating bath of the rotary evaporator is full of water, and all air and water lines are attached.

4. Weigh the empty evaporation and distillate flasks and securely clamp them to the assembly.
5. Turn on the heating bath and adjust the temperature set point to 55 oC. Turn on the water supply to the condenser. Place a bowl of ice underneath the distillate flask.
6. Using graduated cylinders, measure out 40 mL of acetone and 20 mL of water. Record the weight and volume of this mixture. Pour the mixture into the evaporation flask.
7. Set the rotation level to 4 (~250 rpm) and lower the flask into the heating bath.
8. Adjust the pressure set point to 750 mbar and start the vacuum. Let the rotary evaporator run and watch condensation on the condenser. When no droplets are visible, raise the evaporation flask out of the heating bath, stop the rotation and stop the vacuum. Vent the assembly to atmospheric pressure.
9. Weigh the evaporation flask with the remaining liquid. Using graduated cylinders, measure the volume of liquid inside the evaporation flask. Repeat this with the distillate flask. Dump the contents of the flasks into a waste container.
10. Repeat steps (6) to (9) with pressure set points of 700, 650, 600, 550, 450, 350 and 250 mbar. For lower pressures, reduce pressure slowly and rub the condenser walls with ice to prevent solvent leaks.

Safety Issues: Acetone is a known irritant. Personal protective equipment must be used while handling it. Acetone fumes should not be inhaled. While rotary evaporation is underway, watch the droplets on the condenser. If they climb too high, or if they aren’t visible even though evaporation is occurring in the evaporation flask, there may be risk of venting solvent into the pump. In this case, notify your TA, raise the evaporation flask out of the heating bath, and stop the vacuum. In case of any eye contact with chemicals, wash eyes with plenty of water. For further information, check acetone MSDS [4]. Handle glassware with care.

6.3.5. Report Objectives

1. Calculate the densities of the acetone-water mixtures from Procedure step (2). Use densities and molecular weights to find the acetone mole fraction of each mixture. Plot density versus mole fraction and fit a trendline to the data. Report the equation of the fit as well as the coefficient of determination (the R^2 value).
2. Calculate the densities of the acetone-water mixtures from the evaporation flasks from Procedure step (9). Using the equation relating densities to mole fraction, calculate the mole fractions of acetone and water in the flask. These are the x_i values for this experiment.
3. Use the Antoine equation to calculate saturation pressures (P_i^{sat}) for acetone and water at 55 ^{o}C.

4. Derive the relation between P and x_1 introduced in Theory section 6.3.2.2.
5. Estimate the A_{12} and A_{21} parameters which best fulfill this relation given your experimental x_1 and P values, using Microsoft Office Excel Solver or the `lsqcurvefit` or `fminunc` functions in MATLAB.
6. Using the estimated values of A_{12} and A_{21}, as well as Equation 6.3.2, calculate y_1^* values for 200 evenly spaced x_1^* data between 0 and 1. On the same axes, plot P versus x_1^* and P versus y_1^*. This is your pressure-composition graph. Plot your P versus x_1 data on this graph and show your initial composition.
7. Calculate the densities of the acetone-water mixtures from the distillate flasks from Procedure step (9). Using the equation relating densities to mole fraction, calculate the mole fractions of acetone and water in the flask. Plot these values on the pressure-composition graph.

6.3.6. References

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