A Barker Type Approach for Measuring and Interpreting VLE of Polymer Mixed Solvent Systems

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A Barker Type Approach for Measuring and Interpreting VLE of Polymer Mixed Solvent Systems

by

Vaishali Jain

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering Department of Chemical, Biological and Materials Engineering College of Engineering University of South Florida

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Dedication

This thesis is dedicated to my family and friends and my professors for their constant support and motivation.
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Abstract

The environment around us has a great impact on human health. A polluted environment can adversely impact human health and cause diseases like cancer, skin diseases, breathing problems and many more and hence altering the quality of life. Hence it is very important to develop sensors that can efficiently detect these harmful substances from environment. Volatile organic compounds (VOCs) are carbon-based chemical substances that are volatile even at ambient temperature and pressure conditions which enter the atmosphere through industrial processes, building materials, etc.

Acoustic wave devices can detect very low concentrations (ppm, ppb) of organic compounds in the environment. A thin layer of chemically selective material is coated on the surface of the acoustic wave device for the collection of analyte molecules by sorption. The amount of sorption depends upon the physical and chemical properties of the film (typically a polymer) coated on the QCM.

Though the existing technology relates a change in frequency of the sensing element to the total amount of mass sorbed in the coated film. However, if the sorption is from a mixture, the masses of individual analytes cannot be determined from these measurements. The purpose of this work is to propose and test an algorithm for determining the weight fractions of individual analytes in the film from a knowledge of the total weight fraction of sorbed species at equilibrium. The algorithm is an extension of Barker’s method, which is routinely applied to
vapor-liquid equilibrium of small molecules to determine concentrations (in this case, vapor-phase mole fractions) that were not directly measured.
Chapter 1: Introduction

1.1 Motivation

The environment around us has a great impact on human health. A polluted environment can adversely impact human health and cause diseases like cancer, skin diseases, breathing problems and many more and hence altering the quality of life. Hence it is very important to develop sensors that can efficiently detect these harmful substances in the environment.

Volatile organic compounds (VOCs) are carbon-based chemical substances that are volatile even at ambient temperature and pressure conditions. They enter the atmosphere through industrial processes, building materials, household or personal cleaning products, cosmetics, paints, varnishes and waxes, etc. Some examples of VOCs are benzene, toluene, ethyl-benzene, xylene (BTEX), etc.¹⁻³

Though several types of sensors have already been developed for detection of VOCs including gas sensors, optical sensors, and potentiometric sensors, they all have very long fabrication processes and poor outcomes. To accommodate the shortcomings of these existing sensors, surface acoustic wave sensors (SAW) such as quartz crystal microbalance (QCM) are used as chemical sensors. They have better sensitivity, selectivity and short response time along with low cost and ease of manufacturing.⁴⁻⁵

Acoustic wave devices can detect very low concentrations (ppm, ppb) of organic compounds in the environment. A thin layer of chemically selective material is coated on the surface of the acoustic wave device for the collection of analyte molecules by sorption. The
amount of sorption depends upon the physical and chemical properties of the film (typically a polymer) coated on the QCM.

The existing technology relates a change in frequency of the sensing element to the total amount of mass sorbed in the coated film. However, if the sorption is from a mixture, the masses of individual analytes cannot be determined from these measurements. The purpose of this work is to propose and test an algorithm for determining the weight fractions of individual analytes in the film from a knowledge of the total weight fraction of sorbed species at equilibrium. The algorithm is an extension of Barker’s method, which is routinely applied to vapor-liquid equilibrium of small molecules to determine concentrations (in this case, vapor-phase mole fractions) that were not directly measured.

1.2 Previous Work

Many previous works have shown that applying Barker’s method for small molecules in systems comprising two solvents in vapor-liquid equilibrium is more efficient than using other classical methods of parameter estimation because it eliminates the need to experimentally draw vapor phase compositions, which generally have high experimental errors. Instead, total pressure and liquid mole fraction data is used to obtain the activity coefficient model and parameters and hence to calculate vapor phase mole fraction. It has also been demonstrated that these calculations are as accurate as measured experimental data, hence minimizing a great deal of error from the system. The use of this approach has also been extended to system of mixed solvent and non-volatile electrolytes. The reason for attempting to apply it to systems of a mixed solvent in a polymer is that it would be very difficult to measure the individual weight fractions of solvents in a polymer film.
1.3 QCM

Quartz crystal microbalance (QCM) is a mass sensing technique which is based on the piezoelectric effect of quartz crystals. In 1959, a linear relationship between the frequency decrease of oscillating quartz crystal and mass deposited on the crystal, which allowed the use of quartz crystal as a sensing device was reported by Sauerbray. The Sauerbray equation is given by

\[ \Delta f = -2\Delta m f^2 / A (\mu \rho q)^{0.5} = -C_f \Delta m \]  

where,

\( \Delta f \) is the measured resonant frequency shift,

\( f \) is the intrinsic frequency of the crystal,

\( A \) is electrode area,

\( \Delta m \) is the mass change on the crystal,

\( \rho_q \) is the density of the crystal and

\( \mu \) is the shear modulus.

The Sauerbray equation is only valid for small elastic masses and becomes invalid if the mass is inelastic or increases to 2% of mass of crystal. For liquid samples, others factors such as density and viscosity of liquid also need to be considered because there is drastic change in oscillating frequency when a liquid sample interacts with a the crystal. The equation for frequency shift in case of liquid samples is given by

\[ \Delta f = f_0^{3/2} (\rho \eta / \pi \rho_q \mu)^{1/2} \]  

where \( \rho \) and \( \eta \) are the density and viscosity of the liquid respectively.
The basic principle of quartz crystal is based on the oscillation of the crystal at its resonant frequency when alternating voltage is applied. Deposition of mass on the crystal results in frequency shift of QCM.

The frequency shift $\Delta f$ between the purged crystal and the crystal with sorbed solvent is used in conjunction with $\Delta f_0$ to obtain the weight fraction $w_1$ of the solvent via the Sauerbrey equation:

$$w_1=\frac{\Delta f}{\Delta f + \Delta f_0}$$  (3)

where $\Delta f_0$ is the frequency shift due to the mass of polymer film and $\Delta f$ is the frequency shift due to the mass of sorbed solvent as described in equation (1). If more than one species is being sorbed, $w_1$ in equation 1 is the weight fraction of all sorbed species in the film.

A QCM is a piezoelectric device consisting a thin quartz disk coated with an electrode. The quartz crystal disk is either AT cut, or BT cut, such that acoustic wave propagates perpendicularly to the crystal surface.

1.4 Goal/ Thesis Outline

Within the context of this previous work, my thesis concentrates on determining individual solvent weight fractions using total solvent weight fraction, $w_t$ when the polymer film on a QCM is exposed to a mixture of solvents in a vapor phase. The algorithm will be verified through simulations and then applied to experimental data for the sorption of benzene and toluene by poly (ethyl methacrylate) coated onto a QCM crystal. This thesis is organized into 7 chapters. Chapter 1 is the introductory chapter which includes motivation behind the thesis, literature review, and basic concepts about quartz crystal microbalance. Chapter 2 deals with the thermodynamics part of the project explaining the theory behind vapor-liquid equilibrium, Flory Huggins and modified Flory Huggins modeling, activity coefficients and also throwing insight on extension of Barker’s
method. Chapter 3 discusses the simulations used and the logic behind them. Chapter 4 is a detailed discussion of the results of simulations from the previous chapter. Chapter 5 gives a complete description of the apparatus being used and its detailed set up. Chapter 6 presents the experimental results and detailed discussion of these results followed by Chapter 7 which includes conclusions and future work.
Chapter 2: Thermodynamics

2.1 VLE

Vapor-liquid equilibrium is described by equality of fugacities. In order to reach equilibrium, the fugacity of the solvent (1) in a liquid (polymer in this case) phase must be equal to the fugacity of solvent in the vapor phase.\(^\text{11}\)

\[
f_{1 \text{ vapor}} = f_{1 \text{ liquid}} \tag{4}
\]

The fugacity in the vapor can be expressed as a correction to the ideal gas model and the fugacity in the liquid as a correction to the ideal solution model as follows,

\[
y_1 \, P \, \phi_1 = x_1 \, \gamma_1 \, f_{1 \text{ pure}} \tag{5}
\]

where, \(\phi_1\) - fugacity coefficient of solvent in the vapor phase

\(\gamma_1\) - activity coefficient of solvent in the liquid phase

\(y_1\) - mole fraction of solvent in vapor phase

\(x_1\) - mole fraction of solvent in liquid (polymer) phase

\(f_{1 \text{ pure}}\) - fugacity of pure liquid solvent at the temperature of the mixture

\(P\) – total pressure

At low \(P\), vapor phase can be assumed to be an ideal gas and

\[
f_{1 \text{ pure}} \approx P_{1\text{sat}}
\]

where \(P_{1\text{sat}}\) is saturated (vapor) pressure of component 1 at the temperature of the mixture.
So equation (5) can be rewritten as –

\[ y_1 P = x_1 \gamma_1 P_1^{\text{sat}} \]  \hspace{1cm} (6)

Also the activity \( a_1 \) of solvent is defined by, \( a_1 = x_1 \gamma_1 \)

so equation (6) becomes,

\[ a_1 P_1^{\text{sat}} = y_1 P \]  \hspace{1cm} (7)

2.2 Flory Huggins Model (FH)

To apply equation (7) to calculate equilibrium compositions, it is necessary to express the activity \( a_1 \) in terms of composition. In this work, we use Flory Huggins model and a modification to it.

The Flory-Huggins description of the activities in a binary system of solvent (1) and polymer (2) is expressed in terms of the excess Gibb’s free energy by \(^{12}\)

\[ \frac{G^E}{RT} = N_1 \ln (\phi_1/x_1) + N_2 \ln (\phi_2/x_2) + \chi \phi_1 \phi_2 (N_1 + rN_2) \]  \hspace{1cm} (8)

where,

\[ G^E \] - coefficient for excess Gibb’s free energy

\( T \) = temperature of the system

\( R \) = universal gas constant.

\( x_1 \), \( x_2 \) - mole fractions of solvent and polymer

\( \phi_1 \phi_2 \) - volume fractions of solvent and polymer

\( r = V_2/V_1 \) - ratio of molar volumes

\( N_1 \), \( N_2 \) - number of moles of solvent and polymer

\( \chi \) - adjustable parameter

The resulting Flory-Huggins equation for the activity of solvent 1 in a polymer-solvent
binary system is given as:

\[ \ln a_1 = \ln \phi_1 + (1 - V_1/V_2) \phi_2 + \chi \phi_2^2 \]  

(9)

where, \( a_1 \) = - activity of solvent

Volume fractions of solvent and polymer can be calculated from the following relations

\[ \phi_1 = V_1 x_1 / (V_1 x_1 + V_2 x_2) \]

\[ \phi_p = V_2 x_2 / (V_1 x_1 + V_2 x_2) \]

where, \( x_1 \) and \( x_2 \) - mole fractions of solvent and polymer.

The equation for a binary system can be extended to a ternary system of two solvents (component 1 and component 2) and polymer (component 3) as follows,

\[ \ln a_1 = \ln \phi_1 + (1 - \phi_1) - (V_1 \phi_2/V_2) - (V_1 \phi_3/V_3) + (x_{12} \phi_2 + x_{13} \phi_3)(1 - \phi_1) - x_{23} \phi_2 \phi_3 \]  

(10)

\[ \ln a_2 = \ln \phi_2 + (1 - \phi_2) - (V_2 \phi_1/V_1) - (V_2 \phi_3/V_3) + (V_2/V_1)(x_{12} \phi_1 + x_{23} \phi_3)(1 - \phi_2) - (V_2/V_1)x_{13} \phi_1 \phi_3 \]  

(11)

where \( x_{12}, x_{23} \) and \( x_{13} \) are adjustable parameters

\[ x_i = \text{mole fractions of i} \]

\[ \phi_i = \text{volume fraction of i} \]

\[ V_i = \text{molar volume of i} \]

Also,

\[ \phi_1 = V_1 x_1 / V_1 x_1 + V_2 x_{12} + V_3 x_3 \]

\[ \phi_2 = V_2 x_2 / V_1 x_1 + V_2 x_{12} + V_3 x_3 \]

\[ \phi_3 = V_3 x_3 / V_1 x_1 + V_2 x_{12} + V_3 x_3 \text{ or } \phi_3 = 1 - \phi_1 - \phi_2 \]

To apply the above equation, we require the information regarding the molar volumes, volume fractions and interaction parameters of all three entities in the considered system. Since in experiments we measure the weight fractions of solvents, it is convenient to relate \( \phi_i \) to weight fractions \( (w_i) \):
\[ w_i = (\phi_1 \text{mw}_i/V_i)/ (\phi_1 \text{mw}_1/V_1) + (\phi_2 \text{mw}_2/V_2) + (\phi_3 \text{mw}_3/V_3) \]  

(12)

where \( \text{mw}_i \) = molecular weight of \( i \)

### 2.3 Modified Flory Huggins Model (MFH)

For many systems, the Flory Huggins model is not adequate to fit data to within experimental error and we require a more sophisticated model. In this work we will apply a modification to the existing Flory Huggins model:

\[
\frac{G^E}{RT} = x_1 \ln \left( \frac{\phi_1}{x_1} \right) + x_2 \ln \left( \frac{\phi_2}{x_2} \right) + x_3 \ln \left( \frac{\phi_3}{x_3} \right) + \phi_1 \phi_2 (x_1 + r_2 x_2 + r_3 x_3)(A_{12} \phi_1 + A_{21} \phi_2 + \phi_1
\phi_3(x_1 + r_2 x_2 + r_3 x_3)(A_{13} \phi_1 + A_{31} \phi_3) + \phi_3 \phi_2 (x_1 + r_2 x_2 + r_3 x_3)(A_{23} \phi_2 + A_{32} \phi_3) +
\phi_1 \phi_2 \phi_3 (x_1 + r_2 x_2 + r_3 x_3) C
\]

(13)

where \( A_{12}, A_{21}, A_{23}, A_{32}, A_{13}, A_{31} \) and \( C \) are adjustable parameters,

\[
\frac{r_2}{V_2} = V_1/V_1
\]

\[
\frac{r_3}{V_3} = V_1/V_1
\]

\[
\phi_1 = x_1/ x_1 + r_2 x_2 + r_3 x_3
\]

\[
\phi_2 = x_2 r_2/ x_1 + r_2 x_2 + r_3 x_3
\]

\[
\phi_3 = x_3 r_3/ x_1 + r_2 x_2 + r_3 x_3
\]

Now after differentiating equation (13) with respect to moles of the respective component, we obtain expressions for the activities of the individual species:

\[
\ln a_1 = \ln \left( \frac{\phi_1}{x_1} \right) + (1- \phi_1) - (\phi_2/r_2) - (\phi_3/r_3) + 2 \phi_2 (A_{12} \phi_1 + A_{21} \phi_2)(1- \phi_1) - A_{21} \phi_2^2 + 2 \phi_3 (A_{13} \phi_1 + A_{31} \phi_3)(1- \phi_1) - A_{31} \phi_3^2 - 2 \phi_2 \phi_3 (A_{23} \phi_2 + A_{32} \phi_3) + C \phi_2 \phi_3 (1-2 \phi_1)
\]

(14)

\[
\ln a_2 = \ln (\phi_2 / x_2) + (1- \phi_2) - (\phi_1 r_2) - (\phi_3 r_2/r_3) + r_2[ 2 \phi_3 (A_{23} \phi_2 + A_{32} \phi_3)(1- \phi_2) - A_{32} \phi_3^2 + 2 \phi_1 (A_{12} \phi_1 + A_{13} \phi_3)(1- \phi_2) - A_{12} \phi_1^2 - 2 \phi_1 \phi_3 (A_{13} \phi_1 + A_{31} \phi_3) + C \phi_1 \phi_3 (1-2 \phi_2)]
\]

(15)

\[
\ln a_3 = \ln (\phi_3 / x_3) + (1- \phi_3) - (\phi_1 r_3) - (\phi_2 r_3/r_2) + r_3[ 2 \phi_1 (A_{13} \phi_1 + A_{31} \phi_3)(1- \phi_2) - A_{13} \phi_1^2 + 2 \phi_2 (A_{23} \phi_2 + A_{32} \phi_3)(1- \phi_3) - A_{23} \phi_2^2 - 2 \phi_1 \phi_2 (A_{12} \phi_1 + A_{21} \phi_2) + C \phi_1 \phi_2 (1-2 \phi_3)]
\]

(16)
It should be noted that the Flory Huggins model contains only three binary parameters. The Modified Flory Huggins model contains six binary parameters and one ternary parameter C that can’t be obtained from binary data.

2.4 Barker Method for VLE of Small Molecules

In order to appreciate the extension of Barker’s method, we are first going to review how it is applied to a system of small molecules.

For a binary system with solvents 1 and 2 in vapor-liquid equilibrium, equation (5) can be rewritten as equations (18) and (19) and used to calculate activity coefficients and the excess Gibbs free energy:

\[
y_1 P = \gamma_1 x_1 P_{1 \text{sat}} \quad (17)
\]
\[
y_2 P = \gamma_2 x_2 P_{2 \text{sat}} \quad (18)
\]
\[
y_1 P / x_1 P_{1 \text{sat}} = \gamma_1 \quad \text{and} \quad y_2 P / x_2 P_{2 \text{sat}} = \gamma_2
\]
\[
G^E / RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (19)
\]

where,

- \( y_i \) is mole fraction in vapor phase
- \( x_i \) is mole fraction in liquid phase
- \( P \) is pressure of system
- \( P_{i \text{sat}} \) is saturated vapor pressure of solvent \( i \)
- \( \gamma_i \) is activity of solvent

In classical approach, we measure \( y_i, x_i \) and \( P \) at constant temperature, \( T \) which are used to calculate \( \gamma_i \) and further calculate \( G^E / RT \) using equation (19).

Further the above data obtained is fit to a model for \( G^E / RT \) to obtain adjustable parameters in the model (for instance \( A_{12} \) and \( A_{21} \) in the modified Flory Huggins equation described in section
by minimizing the sum of squares between the experimental values of $G^E/RT$ and those calculated from the model

$$\text{Sum of squares (SOS)} = \sum [(G^E/RT)_{\text{exp} i} - (G^E/RT)_{\text{model i}}]^2$$

So basically the classical method uses $y_i, x_i$ and P to estimate the parameters. The major drawback of this approach is the vapor phase compositions have largest experimental errors.

Hence the Barker method comes into picture here, it does not use $y_i$ for parameter estimation instead only P and $x_i$ data which is used which is explained as follows.

Adding equation (17) and (18), we obtain

$$y_1P + y_2P = \gamma_1 x_1 P_1^{\text{sat}} + \gamma_2 x_2 P_2^{\text{sat}}$$

We know sum of mole fractions in a mixture is always equal to 1. Hence,

$$y_1 + y_2 = 1,$$

hence,

$$P_{\text{calculated}} = \gamma_1 x_1 P_1^{\text{sat}} + \gamma_2 x_2 P_2^{\text{sat}} \quad (20)$$

Now after substituting model for activity coefficients $\gamma_i$, the following sum of squares is minimized to obtain parameters of the model,

$$\text{SOS} = \sum [(P)_{\text{exp} i} - (P)_{\text{modified i}}]^2 \quad (21)$$

Once parameters in activity coefficient model are known, we can calculate $y_1$ and $y_2$ using the following-

$$y_1 = \gamma_1 x_1 P_1^{\text{sat}} / P \quad (22)$$

$$y_2 = \gamma_2 x_2 P_2^{\text{sat}} / P \quad (23)$$

Hence, we don’t really need vapor phase compositions but can simply calculate them at the end. The algorithm for applying Barker’s method to VLE of small molecules is shown in the
2.5 Barker Type Algorithm for Polymer Solvent System

In the current work we study the sorption of a binary solvent mixture (species 1 and 2) into a polymer (3) film. From experiment, we have available the temperature, pressure, vapor phase mole fractions $y_1$ and $y_2$ and the total weight fraction $w_t = (w_1 + w_2)$ of solvents in the polymer. The individual weight fractions of solvents 1 and 2 in the polymer film are not known. A flow sheet for an algorithm to fit these data to an activity model and to recover the individual weight fractions $w_1$ and $w_2$ is shown in figure 2.
Figure 1 The algorithm for applying Barker’s method to VLE of small molecules
Figure 2 The algorithm for applying Barker’s type method to recover $w_1$ and $w_2$
Chapter 3: Simulations and Methodology

There are no experimental data available for measured individual weight fractions of each component in a mixture of various solvents and a polymer, so the approach used here cannot be tested on actual experimental data. The only way to do so is through simulations. Hence several sets of simulated data are created to test the algorithm’s ability to predict individual solvent weight fractions. Further, different noise levels are added to the data sets created to simulate experimental error.

3.1 Data Sheets

To prepare simulated data, two data sheets are first created using Microsoft excel - one for the Flory Huggins model and the other for the modified Flory Huggins model. This results in one set of data that conforms to the Flory-Huggins model and another set which requires a more sophisticated model than the Flory-Huggins equation. Each data set basically contained the following columns: \( r \) which is the ratio of \( \phi_2 / \phi_1 \). Five values of \( r \) are taken which are - 0,1/3 ,1, 3, \( \infty \). The first and last of these refer to the binary 1-3 and binary 2-3 systems, respectively. Corresponding to each value of \( r \), ten values of \( \phi_3 \) are taken that are – 0.81, 0.83,0.85,............,0.99. Hence we get 50 rows. Now for each row, \( \phi_1 \) and \( \phi_2 \) are calculated using the expressions-

\[
\phi_1 + \phi_2 + \phi_3 = 1 \quad \text{and} \quad r = \frac{\phi_2}{\phi_1}
\]

After we get \( \phi_1 \) and \( \phi_2 \), equation (10) and (11) are used to calculate \( a_1 \) and \( a_2 \) Further equation (7) is used to calculate \( y_1 \) and \( y_2 \) which are in turn used to calculate \( w_1 \) and \( w_2 \) using equation (12) and hence \( w_1 + w_2 = w_{\text{total}} \)
For the above calculations, the system is modeled on the benzene and toluene solvent system in polymer PEMA. So the values of various parameters were already known and used to make the above calculations:

Component 1 - benzene
Component 2 – toluene
Component 3 - PEMA

Temperature of system, $T = 25$ Celsius

Pressure, $P=1$ atm

For Flory Huggins model, the parameters are:

Molar volumes, $V_1, V_2, V_3 = 88, 106, 305932$ cm$^3$/mol

Saturated pressures, $P_1^{sat} = 0.118$ and $P_2^{sat} = 0.03513$ atm

Molecular weights of component 1,2,3 = 78.11, 92.14, 340000 g/mol respectively

Adjustable parameters are assumed to be

$x_{12} = 0.1$

$x_{13} = 0.255$

$x_{23} = 0.478$

To illustrate what the excel sheet looks like, a screenshot of one of the excel sheets is shown in figure 3.
The data sets described above are called “perfect” data because they are generated from a model with known parameters. To test the algorithm, the data should be reflective of real experimental data and include experimental error. Thus, additional data sets are created by adding noise to previous perfect data. To do so first of all a random number is assumed between 0 to 1. Further 1-2*random number is calculated. Then $y_1$ noise is calculated as

$$y_1\text{ noise} = y_1 + \text{noise level} \cdot y_1 \cdot (1-2\times\text{random number})$$

Similarly, noise is added to $y_2$ and $w_1$ and $w_2$ and data sets were created with three levels of noise: 0.01, 0.05, 0.1.

For the modified Flory Huggins model, the system specifications are as follows:

Component 1- benzene
Component 2 – dichloromethane
Component 3- PMMA

Molar volumes, $V_1$, $V_2$, $V_3 = 64.44$, 92.41, 156800 cm$^3$/mol

Saturated pressures, $P_{1\text{sat}} = 0.125$ and $P_{2\text{sat}} = 0.546$ atm
Molecular weights of component 1,2,3 = 84.93, 78.11, 185000 kg/mol respectively

The adjustable parameters are assumed to be-

\[ A_{12} = -0.027 \]
\[ A_{21} = -0.07 \]
\[ A_{23} = 0.551 \]
\[ A_{32} = 0.212 \]
\[ A_{13} = 0.714 \]
\[ A_{31} = 0.081 \]
\[ C = 0.7 \]

3.2 MATLAB Simulation

Similarly, two MATLAB codes are written (available in appendix), one for the FLORY HUGGINS model and other for the modified FLORY HUGGINS model. The code basically regresses the \( y_1, y_2 \) and \( w_{\text{total}} \) data from excel sheets to obtain the adjustable parameters in the activity model which in turn are used to calculate individual weight fraction of solvents, \( w_1 \) and \( w_2 \). If no noise was added to the data, the model should recover the exact parameters used to compute the data set and the exact solvent mole fractions in the data set. When noise is added to the data, the calculated parameters and solvent mole fractions would not necessarily be recovered. In fact, the goal here is to see how well they can be recovered.

Various MATLAB runs are made using the data sheets made as described in the above section and codes written.

The first run is made by running MATLAB code for the Flory-Huggins model on the data sheet created using the Flory-Huggins Model.
The next run is made by running the data sheet made for modified Flory Huggins model in the MATLAB code made for modified Flory Huggins model, for the following cases -

1) All 7 adjustable parameters are floating.
2) $A_{12}$ and $A_{21}$ are fixed and the remaining 5 parameters are floating.
3) Finding first the binary parameters ($A_{13}$, $A_{31}$, $A_{23}$, $A_{32}$) from binary data and substituting them along with $A_{12}$ and $A_{21}$ into code for the ternary data, which is then used to find the parameter C from ternary data.

The reason for running three different cases above is to demonstrate the different ways that can be used to generate parameters, and hence compare them and decide which is best way to proceed.

Then, the next run is made by running the data sheet made for the modified Flory Huggins model in the MATLAB code made for Flory Huggins model. This case shows the effect of underfitting the data.

Then, the next run is made by running the data sheet made for the Flory Huggins model in the MATLAB code made for modified Flory Huggins model, for the following cases –

1) All 7 adjustable parameters are floating
2) $A_{12}$ and $A_{21}$ are fixed and rest 5 parameters are floating
3) Finding first the binary parameters ($A_{13}$, $A_{31}$, $A_{23}$, $A_{32}$) from binary data and substituting them along with $A_{12}$ and $A_{21}$ into code for the ternary data, which is then used to find the parameter C from ternary data.

These cases show the effect of overfitting the data.

Ultimately the output for these all runs gives the following data:

Residual ($w_{\text{experimental}} - w_{\text{calc}}$), activity coefficients, adjustable parameters, $w_1$, $w_2$
Chapter 4: Simulation and Results

4.1 Simulation Results

This chapter gives the overview results of the cases described in chapter 3. It discusses the results of over fitting and under fitting data and the best ways of obtaining parameters in a model with both binary and ternary parameters. I basically made four sets of data sheets for each noise level 0.01, 0.05, 0.1 by using different random number sets. This was done to obtain more reliable statistics for a given noise level. However, there were no major variations in results among those four data sets for each level of noise. To illustrate the results given by above-mentioned simulations, all graphs from runs with noise=0.1 are demonstrated in the next section. Below are the tables showing the average residual in $w_1$ and $w_2$ and the average bias in $w_1$ and $w_2$ for all the four data sets for noise $n=0.1$ for each different cases. Also, the calculations in the tables are made as follows:

\[
\text{Avg bias } w_1 = \frac{\sum (w_{1\text{cal}}-w_1)}{n} \]

\[
\text{Avg residual } w_1 = \frac{\sum |w_{1\text{cal}}-w_1|}{n} \]

\[
\text{Avg bias } w_2 = \frac{\sum (w_{2\text{cal}}-w_2)}{n} \]

\[
\text{Avg residual } w_2 = \frac{\sum |w_{2\text{cal}}-w_2|}{n} \]
Table 1 Results of fitting the Flory-Huggins model to data created using the Flory-Huggins model

<table>
<thead>
<tr>
<th>Set no</th>
<th>Avg bias $w_1$</th>
<th>Avg residual $w_1$</th>
<th>Avg bias $w_2$</th>
<th>Avg residual $w_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00121</td>
<td>0.00402</td>
<td>-0.00176</td>
<td>0.00524</td>
</tr>
<tr>
<td>2</td>
<td>0.00045</td>
<td>0.00330</td>
<td>-9.1E-06</td>
<td>0.00297</td>
</tr>
<tr>
<td>3</td>
<td>-0.00031</td>
<td>0.00252</td>
<td>0.00071</td>
<td>0.00425</td>
</tr>
<tr>
<td>4</td>
<td>0.00013</td>
<td>0.00292</td>
<td>-0.00060</td>
<td>0.00289</td>
</tr>
<tr>
<td>average</td>
<td>0.00052</td>
<td>0.00319</td>
<td>0.00076</td>
<td>0.00383</td>
</tr>
</tbody>
</table>

For Table 1, average residuals in $w_1$ and $w_2$ are both at level experimental error 0.004 for noise level (0.1) and bias are small too. Bias are about 15-20% of average residual. Hence the method works well.

Table 2 Results of fitting modified Flory Huggins model with all 7 parameters floating to data created for modified Flory Huggins model

<table>
<thead>
<tr>
<th>Set no</th>
<th>Avg bias $w_1$</th>
<th>Avg residual $w_1$</th>
<th>Avg bias $w_2$</th>
<th>Avg residual $w_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.00235</td>
<td>0.00454</td>
<td>0.00259</td>
<td>0.00429</td>
</tr>
<tr>
<td>2</td>
<td>-0.00016</td>
<td>0.00375</td>
<td>6.6E-05</td>
<td>0.00320</td>
</tr>
<tr>
<td>3</td>
<td>-0.00136</td>
<td>0.0051</td>
<td>0.00087</td>
<td>0.00334</td>
</tr>
<tr>
<td>4</td>
<td>0.00037</td>
<td>0.00335</td>
<td>-0.00032</td>
<td>0.00255</td>
</tr>
<tr>
<td>average</td>
<td>0.00106</td>
<td>0.004185</td>
<td>0.00096</td>
<td>0.00334</td>
</tr>
</tbody>
</table>
Table 3 Results for fitting modified Flory Huggins with 5 floating parameters model to data created for modified Flory Huggins model

<table>
<thead>
<tr>
<th>Set no</th>
<th>Avg bias w₁</th>
<th>Avg residual w₁</th>
<th>Avg bias w₂</th>
<th>Avg residual w₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.002</td>
<td>0.00471</td>
<td>0.00208</td>
<td>0.00398</td>
</tr>
<tr>
<td>2</td>
<td>0.00022</td>
<td>0.004</td>
<td>-0.00016</td>
<td>0.00329</td>
</tr>
<tr>
<td>3</td>
<td>-0.00121</td>
<td>0.00531</td>
<td>0.00093</td>
<td>0.00332</td>
</tr>
<tr>
<td>4</td>
<td>0.00041</td>
<td>0.00334</td>
<td>-0.00053</td>
<td>0.00254</td>
</tr>
<tr>
<td>average</td>
<td>0.00096</td>
<td>0.00434</td>
<td>0.00092</td>
<td>0.00328</td>
</tr>
</tbody>
</table>

Table 4 Results for fitting modified Flory Huggins fitting binary first and then finding parameter c model to data created for modified Flory Huggins model

<table>
<thead>
<tr>
<th>Set no</th>
<th>Avg bias w₁</th>
<th>Avg residual w₁</th>
<th>Avg bias w₂</th>
<th>Avg residual w₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.00167</td>
<td>0.00479</td>
<td>0.00120</td>
<td>0.00342</td>
</tr>
<tr>
<td>2</td>
<td>0.00069</td>
<td>0.00403</td>
<td>-0.00114</td>
<td>0.00352</td>
</tr>
<tr>
<td>3</td>
<td>-0.003</td>
<td>0.00627</td>
<td>0.00090</td>
<td>0.00335</td>
</tr>
<tr>
<td>4</td>
<td>0.00016</td>
<td>0.00328</td>
<td>-0.00050</td>
<td>0.00253</td>
</tr>
<tr>
<td>average</td>
<td>0.00138</td>
<td>0.00459</td>
<td>0.00093</td>
<td>0.0032</td>
</tr>
</tbody>
</table>

For Tables 2 through 4, average residuals in w₁ and w₂ are both within experimental error range level 0.004 approximately for noise level (0.1) and bias are smaller for w₁ for table 2 and table 3 than table 4. Bias is about 20-30% of average residual. Hence the results are roughly equivalent for all three cases and all are acceptable.
Table 5 Results for fitting modified Flory Huggins model, with all 7 parameters floating to data created for Flory Huggins model

<table>
<thead>
<tr>
<th>Set no</th>
<th>Avg bias w₁</th>
<th>Avg residual w₁</th>
<th>Avg bias w₂</th>
<th>Avg residual w₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.0012</td>
<td>0.00385</td>
<td>0.00149</td>
<td>0.00482</td>
</tr>
<tr>
<td>2</td>
<td>-0.00019</td>
<td>0.00331</td>
<td>0.00019</td>
<td>0.00292</td>
</tr>
<tr>
<td>3</td>
<td>-0.00186</td>
<td>0.00314</td>
<td>0.00171</td>
<td>0.00450</td>
</tr>
<tr>
<td>4</td>
<td>-0.00235</td>
<td>0.00341</td>
<td>0.00237</td>
<td>0.00371</td>
</tr>
<tr>
<td>Average</td>
<td>0.0014</td>
<td>0.00342</td>
<td>0.00144</td>
<td>0.00398</td>
</tr>
</tbody>
</table>

Table 6 Results for fitting modified Flory Huggins model, with 5 floating parameters to data created for Flory Huggins model

<table>
<thead>
<tr>
<th>set no</th>
<th>Avg bias w₁</th>
<th>Avg residual w₁</th>
<th>Avg bias w₂</th>
<th>Avg residual w₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.00119</td>
<td>0.00384</td>
<td>0.00148</td>
<td>0.00482</td>
</tr>
<tr>
<td>2</td>
<td>-9.1E-05</td>
<td>0.00335</td>
<td>0.00019</td>
<td>0.003</td>
</tr>
<tr>
<td>3</td>
<td>-0.00223</td>
<td>0.00358</td>
<td>0.00219</td>
<td>0.00483</td>
</tr>
<tr>
<td>4</td>
<td>-0.00184</td>
<td>0.00347</td>
<td>0.00198</td>
<td>0.00318</td>
</tr>
<tr>
<td>average</td>
<td>0.00133</td>
<td>0.00356</td>
<td>0.00146</td>
<td>0.00395</td>
</tr>
</tbody>
</table>
Table 7 Results for fitting modified Flory Huggins model, fitting binary first and then finding parameter c to data created for Flory Huggins model

<table>
<thead>
<tr>
<th>Set no</th>
<th>Avg bias $w_1$</th>
<th>Avg residual $w_1$</th>
<th>Avg bias $w_2$</th>
<th>Avg residual $w_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.8E-05</td>
<td>0.00368</td>
<td>-0.00125</td>
<td>0.00446</td>
</tr>
<tr>
<td>2</td>
<td>0.00136</td>
<td>0.0034</td>
<td>-0.00487</td>
<td>0.00570</td>
</tr>
<tr>
<td>3</td>
<td>-0.00245</td>
<td>0.00478</td>
<td>-0.00119</td>
<td>0.00411</td>
</tr>
<tr>
<td>4</td>
<td>-0.00073</td>
<td>0.00316</td>
<td>-0.00125</td>
<td>0.00412</td>
</tr>
<tr>
<td>average</td>
<td>0.00113</td>
<td>0.00375</td>
<td>0.00214</td>
<td>0.00459</td>
</tr>
</tbody>
</table>

For Tables 5 through 7, these are cases for over-fitting and average residuals in $w_1$ and $w_2$ are both within experimental error range 0.004 approximately noise level (0.1). Hence the results are roughly equivalent for all three cases and all are acceptable. Bias are also mostly similar for table 5, table 6 and table 7. But fit c gives larger bias for $w_2$.

Table 8 Results for fitting Flory Huggins model to data created for modified Flory Huggins model

<table>
<thead>
<tr>
<th>Set no</th>
<th>Avg bias $w_1$</th>
<th>Avg residual $w_1$</th>
<th>Avg bias $w_2$</th>
<th>Avg residual $w_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.00011</td>
<td>0.00475</td>
<td>-0.00235</td>
<td>0.00514</td>
</tr>
<tr>
<td>2</td>
<td>-0.00286</td>
<td>0.00607</td>
<td>0.00046</td>
<td>0.00375</td>
</tr>
<tr>
<td>3</td>
<td>-2.8E-05</td>
<td>0.00508</td>
<td>-0.00136</td>
<td>0.00396</td>
</tr>
<tr>
<td>4</td>
<td>-0.00396</td>
<td>0.00686</td>
<td>0.00111</td>
<td>0.00304</td>
</tr>
<tr>
<td>average</td>
<td>0.00173</td>
<td>0.00569</td>
<td>0.00132</td>
<td>0.00397</td>
</tr>
</tbody>
</table>
Table 8 represents the case of under-fitting, residual in $w_1$ is not within experimental error 0.004, which is expected in this case because the model used is not sophisticated enough, but surprisingly bias is not too large. Bias is about 30\% of average residual for both $w_1$ and $w_2$. Now to understand more about each of these methods mentioned in above tables 1-8 and to distinguish which method works more efficiently than others lets have a look at the parameter values we obtained from each of these methods. The following tables 9 and 10 give a summary of the parameter values we get from above mentioned cases. Specifically, Table 9 addresses fits of both models to the Flory Huggins data set. The first row shows the parameters used to construct the perfect data sets (before noise was added).

Table 9 Average parameter values from different runs on the FH data sets

<table>
<thead>
<tr>
<th>Data set</th>
<th>MATLAB</th>
<th>A12</th>
<th>A23</th>
<th>A13</th>
<th>A21</th>
<th>A32</th>
<th>A31</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>FH</td>
<td>FH true</td>
<td>0.1</td>
<td>0.478</td>
<td>0.255</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FH</td>
<td>FH</td>
<td>0.444</td>
<td>0.474</td>
<td>0.236</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FH</td>
<td>MFH(7 P)</td>
<td>0.857</td>
<td>0.524</td>
<td>0.027</td>
<td>2.352</td>
<td>0.336</td>
<td>0.335</td>
<td>0.622</td>
</tr>
<tr>
<td>FH</td>
<td>MFH(5 P)</td>
<td>0.1</td>
<td>0.577</td>
<td>0.053</td>
<td>0.1</td>
<td>0.318</td>
<td>0.318</td>
<td>1.197</td>
</tr>
<tr>
<td>FH</td>
<td>MFH(C)</td>
<td>0.1</td>
<td>1.0062</td>
<td>0.1227</td>
<td>0.1</td>
<td>0.2863</td>
<td>0.2831</td>
<td>0.88</td>
</tr>
</tbody>
</table>

*The parameters mentioned in bold are the ones that were already defined for the system and other are the ones calculated using MATLAB*

For the case of fitting FH model in FH data, as clear from above, the $A23$ and $A13$ values are close to the true values which shows that the system is working well while $A12$ value is quite different. The reason behind that is the 1-2 binary is the solvent binary system and that the data
for compositions are well removed from those of that binary system. In fact, that is the reason why we fix A12/A21 values in the MFH 5P and C cases. Now talking about fitting FH data to MFH model (over-fitting), as we can clearly see above that A23/A32 and A13/A31 values are not converging to their true values, In fact, over-fitting the data gives a non-zero value for ternary parameter c when it is not even needed to fit these data. Hence we can conclude that although the fits to data were good as we saw in tables 1-8, the parameter values have no significance for those fits. Hence over-fitting meets the goal of providing reliable individual solvent weight fractions but one would not want to place any significance to the parameter values in the activity model.

Table 10 Average parameter values from different runs on the MFH data sets

<table>
<thead>
<tr>
<th>Data set</th>
<th>MATLAB</th>
<th>A12</th>
<th>A23</th>
<th>A13</th>
<th>A21</th>
<th>A32</th>
<th>A31</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFH</td>
<td>MFH(7 P)</td>
<td>5.582</td>
<td>0.590</td>
<td>0.642</td>
<td>1.111</td>
<td>0.185</td>
<td>0.128</td>
<td>-0.378</td>
</tr>
<tr>
<td>MFH</td>
<td>MFH(5 P)</td>
<td>-0.027</td>
<td>0.600</td>
<td>0.758</td>
<td>-0.07</td>
<td>0.169</td>
<td>0.091</td>
<td>0.785</td>
</tr>
<tr>
<td>MFH</td>
<td>MFH(C)</td>
<td>-0.027</td>
<td>1.0035</td>
<td>0.2180</td>
<td>-0.07</td>
<td>0.0583</td>
<td>0.2260</td>
<td>0.722</td>
</tr>
<tr>
<td>MFH</td>
<td>MFH true</td>
<td>-0.027</td>
<td>0.551</td>
<td>0.714</td>
<td>-0.07</td>
<td>0.212</td>
<td>0.081</td>
<td>0.7</td>
</tr>
</tbody>
</table>

*The parameters mentioned in bold are the ones that were already defined for the system and other are the ones calculated using MATLAB

For the case of fitting MFH data into MFH model, as we can see from above the case with all 7 parameters floating, the parameters values are off and don’t converge to the true values.

For the cases with 5 parameters floating and fitting binary first and then c, the ternary parameter C is much closer to its true value. We can conclude that although all the three cases gave similar residuals and biases, the cases with 5 parameters floating and fitting binary first and then c return parameter values closer to the true values than the case when all 7 parameters are
In conclusion:

1) Under-fitting – (fitting Flory Huggins model to data created using the modified Flory Huggins model). Residual in \( w_1 \) is not within experimental error, which is expected in this case because the model used is not sophisticated enough, but surprisingly the bias is not too large. Bias is about 30% of average residual for both \( w_1 \) and \( w_2 \). Since the fits are not to within experimental error, we can consider using a more complicated model.

2) Over-fitting – (fitting modified Flory Huggins model to data created using the Flory Huggins model). Regressed A23 and A13 values are similar to their true values and even predict a nonzero value for the ternary parameter when one is not needed to fit the data. However, values of \( w_1 \) and \( w_2 \) are predicted within experimental error.

3) For the case of fitting MFH data into MFH model, for the case with all 7 parameters floating, the regressed parameter values are different from their true values. While for the cases with 5 parameter floating and fitting binary first and then c, the parameter values converge better to their true values. So we can conclude that, though all the three cases gave similar residuals and were good fits, the cases with 5 parameter floating and fitting binary first and then c are better than the approach in which all 7 parameter float for returning parameter values closer to their true values.

To better illustrate the above conclusions and results seen in tables 1-10, the graphs between residuals in \( w_1/w_2 \) and \( w_t \) are shown on next pages in figures 4-19, for all the above-mentioned cases.

For the following graphs in figure 4-19, the x-axis has the \( w_t \) points from simulated excel sheets data. The y-axis has either \( w_1 \) or \( w_2 \) residual (\( w_i \) generated from MATLAB
minus \( w_i \) from simulated excel data).

1) Case 1 - running the data sheet made for Flory Huggins model in MATLAB made for Flory Huggins model.

Figure 4 Residuals in \( w_1 \) as function of total weight fraction

Figure 5 Residuals in \( w_2 \) as function of total weight fraction
Figure 4-5 show residuals for set 1 in table 1 and both residuals are essentially bias free. Fits are about the level of expected experimental error.

2) Case 2 - running the data sheet made for modified Flory Huggins model in MATLAB made for modified Flory Huggins model for case where all 7 adjustable parameters are floating.

Figures 6 and 7 show the residuals for set 1 in table 2. Fits are mostly about the level of experimental error. The bias are equally scattered around zero line for all values of $r$ for $w_1$. Though there is couple of isolated points on both graphs.
3) Case 3- running the data sheet made for modified Flory Huggins model in MATLAB made for modified Flory Huggins model for case where $A_{12}$ and $A_{21}$ are fixed and rest 5 parameters are floating
Figures 8 and 9 show the residuals for set 1 from table 3. They are mostly within the experimental error range. Bias are mostly small. $w_2$ has positive bias. Though there are couple of isolated points on both graphs.

4) Case 4- running the data sheet made for modified Flory Huggins model in MATLAB made for modified Flory Huggins model for case where only binary parameters that is $A_{13}$, $A_{31}$, $A_{23}$, $A_{32}$ are first found and then substituting them along with known $A_{12}$ and $A_{21}$ values to find the parameter $C$. 

Figure 9 Residuals in $w_2$ as function of total weight fraction
Figures 10 and 11 show the residuals for set 1 from table 4. They are mostly within the experimental error range. Bias are mostly small. \( w_2 \) has positive bias. Though there are couple of isolated points on both graphs.
5) Case 5- running the data sheet made for modified Flory Huggins model in MATLAB made for Flory Huggins model

Figure 12 Residuals in $w_1$ as function of total weight fraction

Figure 13 Residuals in $w_2$ as function of total weight fraction
Figures 12 and 13 show the residuals for set 1 from table 5. They are mostly within the experimental error range. Bias is mostly small for both graphs. Though both graphs have couple of isolated points.

6) Case 6- running the data sheet made for Flory Huggins model in MATLAB made for modified Flory Huggins model for case where all 7 adjustable parameters are floating

![Figure 14](image1.png)

Figure 14 Residuals in $w_1$ as function of total weight fraction

![Figure 15](image2.png)

Figure 15 Residuals in $w_2$ as function of total weight fraction
Figures 14 and 15 show the residuals for set 1 from table 6. They are mostly within the experimental error range. Bias is mostly small. $w_2$ has positive bias. Though there are couple of isolated points on both graphs.

7) Case 7- running the data sheet made for Flory Huggins model in MATLAB made for modified Flory Huggins model for case where $A_{12}$ and $A_{21}$ are fixed and rest 5 parameters are floating.

![Figure 16 Residuals in $w_1$ as function of total weight fraction](image)

![Figure 17 Residuals in $w_2$ as function of total weight fraction](image)
Figures 16 and 17 show the residuals for set 1 from table 7. They are mostly within the experimental error range. Bias is mostly small. Though there are couple of isolated points on both graphs.

8) Case 8- running the data sheet made for Flory Huggins model in MATLAB made for modified Flory Huggins model for case where only binary parameters that is $A_{13}$, $A_{31}$, $A_{23}$, $A_{32}$ are first found and then substituting them along with known $A_{12}$ and $A_{21}$ values to find the parameter C.

Figure 18 Residuals in $w_1$ as function of total weight fraction
Figures 18 and 19 show the residuals for set 1 from table 8. They are mostly within the experimental error range. Bias is mostly small. Though there are couple of isolated points on both graphs.
Chapter 5: Experimental Set-up

The main aim for performing these experiments is to apply the algorithm described in Chapter 2 and tested on simulated data in Chapter 4 to a set of actual experimental $y_1, y_2, w_1$ data to obtain individual weight fractions $w_1$ and $w_2$. The system considered is benzene (1)+toluene (2)+PEMA (3)

5.1 Materials and Methods

Solvents benzene and toluene with 99% purity are purchased from Sigma Aldrich. Poly (ethyl methacrylate) (PEMA) with a molecular mass of 340000 g/mol is purchased from Sigma–Aldrich too. Its structure is shown in figure 20. AT-cut quartz crystals with 5MHz frequency, supplied by Philips Technologies are used. The electrode has a wrap around design which allows the crystal to make electrical contact from one side. The electrode can either be made of gold or silver metal. In this study, a quartz crystal with a gold electrode is used. The diameter of the electrode is approximately 0.5 inch. Quartz crystals are well polished from both sides and have good piezoelectric, electrical and mechanical properties allowing very high stability and better sensitivity. The optimum operating frequency for crystals is 5 MHz with resistances ranges from 6-10 Ohm. The crystals used here have a diameter of 1-inch and thickness of approximately 0.013 inch.
5.2 Apparatus

The apparatus for collecting data for sorption of benzene and toluene has the following sections:

- QCM cell
- Bubblers
- mass flow controllers
- chillers
- Labview /automation

The above-mentioned components are shown below in figures (21-26). The experimental apparatus has been previously discussed in publication by Iyer et. Al.10
Figure 21 Front and back side view of a QCM crystal
Figure 22 Front view of bubblers

Figure 23 Mass flow controller
Figure 24 Image of whole experimental apparatus
5.3 Experimental Procedure

The overall experimental procedure consists of four steps:

- Cleaning of QCM crystal
- Coating of crystal with polymer layer
- Filling up bubblers with desired solvent mixtures
- Data collection

The cleaning process involves removal of any previously deposited polymer film from the QCM. First, the coated crystals are wrapped with Kim Wipes and are placed in a soxhlet extractor. Chloroform solvent is used in the soxhlet extractor to clean the polymer film from the crystal. A condenser is placed on top of the extractor so that the crystal gets cleaned by refluxing. This process takes roughly 6 hours to complete. Then crystals are rinsed with Millipore water and dried off by blowing nitrogen gas on them.

In this project, toluene is taken as solvent to dissolve the polymer (PEMA). A solution of polymer is prepared by adding 0.5g PEMA in 12.5 g (approximately 15 ml) of toluene. This mixture is allowed to sonicate for 1-2 hours and is spin-coated on to a crystal using a Spin coater (shown in Figure 25). The thickness of the coating depends on the speed and time of spin-coating.

In this case, we coated 300μL of solution for an overall period of 5 minutes with speeds of 100 rpm, 1000 rpm, 5000 rpm, 7500 rpm and 10000 rpm by constantly purging with industrial nitrogen. This process leaves us with a frequency shift of 1500-3000 Hz.
Next, all four bubblers are cleaned thoroughly and filled with different mixtures. The first bubbler is filled with pure benzene (20 ml), second is filled with pure toluene (20 ml), third is filled with 1:3 ratio, benzene : toluene (benzene=5 ml, toluene=15 ml) and fourth is filled with 3:1 ratio, benzene : toluene (benzene=15 ml, toluene=5 ml). After that run is complete another run is made with only one bubbler which contains a 1:1 ratio of benzene : toluene (benzene=10 ml, toluene=10 ml).

The experiment and the data collection are automated using software called LabVIEW in which the code can tailored in such a way that the operator can choose the number of data points to be collected per run, choosing the required bubblers of operation, and whether or not to measure a baseline data. The code is written in such a way that the nitrogen gas fed to the mass flow
controllers is controlled to produce flows ranging from 0-100 sccm with increments in 10 sccm summing to a total of 100 sccm. The flow is also routed using normally closed solenoids present at the inlet and the outlet of the impinger. There are 10 different isothermal concentrations that are produced for all the solvent mixtures and are directed towards the cell. The cell consists of a 5MHz QCM crystal and is maintained at room temperature with the help of water chillers. At these conditions, the system is assumed to have reached equilibrium and the sorption data is collected as frequencies along with the calculation of mean, standard deviation and the corresponding weight fractions using Saurbrey’s equation. LABVIEW software is used for data collection in form of frequency, time, resistances and weight fractions. Firstly, the baseline frequency of a bare quartz crystal is measured (5001636.78 Hz) and then data points are collected. The general LABVIEW screen look like as shown in Figure 26. Activity v/s weight fraction curves help us to study the sorption of solvents (benzene, toluene and their mixtures) on the polymer film.
Figure 26 Typical lab-view output
Chapter 6: Results from Experiments

In this chapter, we will fit the Flory Huggins and the modified Flory Huggins models to the experimental data we obtained for the benzene-toluene-PEMA system. Inputs to the algorithm consist of \(y_1\), \(y_2\) and \(w_t\). As before, the output consists of values of the model parameters and of the individual weight fractions \(w_1\) and \(w_2\).

6.1 Flory Huggins Model

First I applied the Flory-Huggins model to the experimental data for benzene (1) – toluene (2) and PEMA (3) using the same algorithm applied to simulated data. Experimental uncertainties in measured weight fractions are estimated to be +/- 0.001. Figure 27 shows the residuals between experimental and calculated total solvent weight fraction. As is evident in Figure 27 that the residuals mostly lie above the zero-line, and the model isn’t bias free it is concluded that the Flory-Huggins model is not really a good model for this system.
Figure 27 Residuals in total solvent weight fraction as function of nitrogen mole fraction in gas phase for FH

6.2 Modified Flory Huggins Model

6.2.1 5-Parameter Floating

Similarly, the below graph shown in Figure 28 represents the modified Flory Huggins model for 5 parameters system where all 5 parameters are made to fit at once. As it is evident in the above graph that the data is evenly scattered above and below the zero-line and also the average residual and average bias are 0.00096 and -0.000017 respectively, which are well within experimental error range. Hence it is a better model for our system representation for calculating weight fractions $w_1$ and $w_2$. 
6.2.2 First Fitting the Binary and Then Fitting C

The below graph shown in Figure 29 represents the modified Flory Huggins model for 5 parameters system where first the binaries are made to fit the model first and at last the ternary parameter c. The data in above graph is also evenly scattered above and below the zero-line and also the average residual and average bias are 0.00096 and -0.000026 respectively, which is mostly similar to the case where all 5 parameters are made to fit at once.
Figure 29 Residuals in total solvent weight fraction as function of nitrogen mole fraction in gas phase for MFH (fitting binary first and then C)

6.3 Adjustable Parameters

The table 11 contains the adjustable parameters from both Flory Huggins and modified Flory Huggins model. A12 and A21 are obtained from fitting MFH model to VLE data for the benzene toluene binary system.

Table 11 Parameter values from different runs

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6.4 Data Showing $w_1$ and $w_2$ Values from MATLAB Run

Table 12 is showing the values of $w_1$ and $w_2$ calculated by fitting the model to $y-w_1$ experimental data. As it concluded in section above that the method of fitting binaries first and then C is better method for finding parameters, so it is used here to calculate $w_1$ and $w_2$.

Table 12 Data from simulation of experimental data in modified Flory Huggins model (fitting binary first and then C)

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53
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Chapter 7: Conclusion and Future Work

7.1 Conclusion

It has been shown that individual weight fractions of each component in two solvent-polymer system can be obtained from total weight fraction data using a Barker-like approach. The algorithm was verified using simulated data and using both the Flory Huggins and the Modified Flory Huggins models. Results from simulations show that we can reproduce \( w_1 \) data within experimental uncertainties and make reliable predictions of the individual solvent weight fractions \( w_1 \) and \( w_2 \). Further experiments were carried out on benzene-toluene-PEMA system using a QCM-based apparatus and the algorithm was applied to calculate individual solvent weight fractions in the polymer from data for the total solvent weight fraction.

7.2 Future Work

Future work includes repeating the same experiment with more than two solvents. The work can be extended to systems with high pressure and taking into consideration the gas phase fugacity coefficients. Moreover the effects of addition of plasticizer and co-polymer can also be further studies. Also the apparatus can be redesigned so that the two solvents are introduced individually and then mixed later rather than by placing a binary mixture in the bubbler.
References


Appendix A: Codes

The code for the FH model follows:

```matlab
clc
clear
global y1 y2 psat1 psat2 res v1 v2 v3 w1 w2 wt iter nw1 nw2 nw3 wtexp act1
act2 a1 a2
iter=0;
T = readtable('noise0.1.xlsx');
y1=T(:,2)'; y2=T(:,3)';
wtexp = T(:,4)';

psat1=0.118;
psat2=.03513;
v1=89.17;
v2=105.91;
v3=306306.3;
nw1=78.11;
nw2=92.14;
nw3=340000;

chiguess = [.1 .478 .255];
%chiguess = [.2 .2 .2];
%chiguess = [-0.27 0.514 0.714];

%uncomment next 2 lines and comment third to get output based on guessed chi values
%Y=sos(chiguess)
%chi=chiguess
chi = fminsearch(@sos,chiguess);
out = [chi(1), chi(2) , chi(3)]
q=[y1' y2' w1' w2' wt' wtexp' res '
fprintf('y1 y2 w1 w2 wt wtexp res

function Y = sos(chi)
global y1 y2 psat1 psat2 res v1 v2 v3 w1 w2 wt iter nw1 nw2 nw3 wtexp act1
act2 a1 a2
global x12 x23 x13
x12 = chi(1);
x23 = chi(2);
x13 = chi(3);
```

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for i=1:50
    a1(i)=y1(i)/psat1;
    a2(i)=y2(i)/psat2;
end

for i=1:30
    act1=a1(i);
    act2=a2(i);
    guess=[.14 .04 .81];
    out=fsolve(@root2d,guess);
    phi1(i)=out(1);
    phi2(i)=out(2);
    phi3(i)=out(3);
end

for j=31:40
    act1=a1(j);
    act2=a2(j);
    guess=[.14 .04 .81];
    out=fsolve(@root2d1,guess);
    phi1(j)=out(1);
    phi2(j)=out(2);
    phi3(j)=out(3);
end

for k=41:50
    act1=a1(k);
    act2=a2(k);
    guess=[.14 .04 .81];
    out=fsolve(@root2d2,guess);
    phi1(k)=out(1);
    phi2(k)=out(2);
    phi3(k)=out(3);
end

for l=1:50
    w1(l)=(phi1(l)*nw1/v1)/(phi1(l)*nw1/v1+phi2(l)*nw2/v2+phi3(l)*nw3/v3);
    w2(l)=(phi2(l)*nw2/v2)/(phi1(l)*nw1/v1+phi2(l)*nw2/v2+phi3(l)*nw3/v3);
    wt(l)=w1(l)+w2(l);
    res(l)=wtexp(l)-wt(l);
end
Y = sum(res.^2);
iter = iter + 1

function F = root2d(x)
global act1 act2
global x12 x23 x13
v1 = 89.17;
v2 = 105.91;
v3 = 306306.3;
    F(1) = -log(act1) + log(x(1)) + (1 - x(1)) - (v1/v2)*x(2) - v1*x(3)/v3 +
          (x12*x(2) + x13*x(3))*(1 - x(1)) - x23*x(2)*x(3);
    F(2) = -log(act2) + log(x(2)) + (1 - x(2)) - v2*x(1)/v1 - v2*x(3)/v3 +
          (v2/v1)*(x12*x(1) + x23*x(3))*(1 - x(2)) - v2*x13*x(1)*x(3)/v1;
    F(3) = 1 - x(1) - x(2) - x(3);
end

function F = root2d1(x)
global act2
global x12 x23 x13
v1 = 89.17;
v2 = 105.91;
v3 = 306306.3;
%x(1) = 0;
    F(1) = x(1);
    F(2) = -log(act2) + log(x(2)) + (1 - x(2)) - v2*x(1)/v1 - v2*x(3)/v3 +
          (v2/v1)*(x12*x(1) + x23*x(3))*(1 - x(2)) - v2*x13*x(1)*x(3)/v1;
    F(3) = 1 - x(1) - x(2) - x(3);
end

function F = root2d2(x)
global act1
global x12 x23 x13
v1 = 89.17;
v2 = 105.91;
v3 = 306306.3;
%x(2) = 0;
    F(1) = -log(act1) + log(x(1)) + (1 - x(1)) - (v1/v2)*x(2) - v1*x(3)/v3 +
          (x12*x(2) + x13*x(3))*(1 - x(1)) - x23*x(2)*x(3);
    F(2) = x(2);
    F(3) = 1 - x(1) - x(2) - x(3);
end

The code for the MFH follows:
clc
clear
global y1 y2 psat1 psat2 res v1 v2 v3 w1 w2 wt iter nw1 nw2 nw3 wtexp r3 r2 act1 act2 a1 a2
iter=0;
T = readtable('n0.1.xlsx');

y1=T(:,2)'; y2=T(:,3)';
wtexp = T(:,4)';

psat1=0.125;
psat2=0.546;
r2=1.434047176;
r3=2433.27126;
v1=64.44;
v2=92.41;
v3=156800;
nw1=84.93;
nw2=78.11;
nw3=185000;

%chiguess = [-0.1214 -4.3701 0.3575 -0.6961 -1.4461 0.5282 -3.5812];
chiguess = [-0.027 .551 .714 -.07 .212 .081 .7];
%chiguess = [.1 .478 .255 .1 .478 .255 .833];
%chiguess = [.68 .68 .68 .68 .68 .68 .68];
%uncomment next 2 lines and comment third to get output based on guessed chi values
%Y=soschi(chiguess)
%chi=chiguess
chi = fminsearch(@soschi,chiguess);
out = [chi(1), chi(2), chi(3), chi(4), chi(5), chi(6), chi(7)]
    % A12 A23 A13 A21 A32 A31 C
fprintf('y1 y2 w1 w2 wt wtexp res \n');
q = [y1' y2' w1' w2' wt' wtexp' res']

function Y = soschi(chi)
global y1 y2 psat1 psat2 res v1 v2 v3 w1 w2 wt iter nw1 nw2 nw3 wtexp r3 r2 act1 act2 a1 a2
global A12 A23 A13 A21 A32 A31 C
A12 = chi(1);
A23 = chi(2);
A13 = chi(3);
A21 = chi(4);
A32 = chi(5);
A31 = chi(6);
C = chi(7);

for i=1:50
    a1(i)=y1(i)/psat1;
a2(i)=y2(i)/psat2;
end

for i=1:30
    act1=a1(i);
    act2=a2(i);
    guess=[.14 .04 .81];
out=fssolve(@roots2d,guess);
phi1(i)=out(1);
phi2(i)=out(2);
phi3(i)=out(3);
end

for j=31:40
    act1=a1(j);
    act2=a2(j);
    guess=[.14 .04 .81];
    out=fssolve(@roots2d1,guess);
    phi1(j)=out(1);
    phi2(j)=out(2);
    phi3(j)=out(3);
end

for k=41:50
    act1=a1(k);
    act2=a2(k);
    guess=[.14 .04 .81];
    out=fssolve(@roots2d2,guess);
    phi1(k)=out(1);
    phi2(k)=out(2);
    phi3(k)=out(3);
end

for l=1:50
    w1(l)=(phi1(l)*nw1/v1)/(phi1(l)*nw1/v1+phi2(l)*nw2/v2+phi3(l)*nw3/v3);
    w2(l)=(phi2(l)*nw2/v2)/(phi1(l)*nw1/v1+phi2(l)*nw2/v2+phi3(l)*nw3/v3);
    wt(l)=w1(l)+w2(l);
    res(l)=wtexp(l)-wt(l);
end

Y=sum(res.^2);
iter = iter+1

function F = root2d(x)
global act1 act2
global A12 A23 A13 A21 A32 A31 C
r2=1.434047176;
r3=2433.27126;
x1=0.5;
x2=0.5;
\[ F(1) = -\log(\text{act1}) + \log(x(1)) + 1 - x(1) - (x(2)/r2) - (x(3)/r3) + \\
(2*x(2)*(1-x(1))*(A12*x(1)) + (A21*x(2))) - (A21*(x(2)^2)) + (2*x(3)*(1-x(1))*(A13*x(1)) + (A31*x(3)))) - (A31*(x(3)^2)) - (2*x(3)*x(2)*((A23*x(2)) + (A32*x(3))))) + (C*x(2)*x(3)*(1-(2*x(1)))); \\
F(2) = -\log(\text{act2}) + \log(x(2)) + 1 - x(2) - (x(1)*r2) - ((x(3)*r2)/r3) + \\
r2*((2*x(3)*(1-x(2))*((A23*x(2)) + (A32*x(3)))) - (A32*(x(3)^2)) + \\
(2*x(1)*(1-x(2))*((A21*x(2)) + (A12*x(1)))) - (A12*(x(1)^2)) - \\
(2*x(3)*x(1)*((A13*x(1)) + (A31*x(3)))) + (C*x(1)*x(3)*(1-(2*x(2)))))); \\
F(3) = 1 - x(1) - x(2) - x(3); \\
\]

\begin{function}
function F = root2d1(x)
global act2
global A12 A23 A13 A21 A32 A31 C
r2=1.434047176;
r3=2433.27126;
x1=0.5;
x2=0.5;
%x(1)=0;
F(1)= x(1);
F(2)= -\log(\text{act2}) + \log(x(2)) + 1 - x(2) - (x(1)*r2) - ((x(3)*r2)/r3) + \\
r2*((2*x(3)*(1-x(2))*((A23*x(2)) + (A32*x(3)))) - (A32*(x(3)^2)) + \\
(2*x(1)*(1-x(2))*((A21*x(2)) + (A12*x(1)))) - (A12*(x(1)^2)) - \\
(2*x(3)*x(1)*((A13*x(1)) + (A31*x(3)))) + (C*x(1)*x(3)*(1-(2*x(2)))))); \\
F(3) = 1-x(1)-x(2)-x(3);
end

function F = root2d2(x)
global act1
global A12 A23 A13 A21 A32 A31 C
r2=1.434047176;
r3=2433.27126;
x1=0.5;
x2=0.5;
%x(2)=0;
F(1)= -\log(\text{act1}) + \log(x(1)) + 1 - x(1) - (x(2)/r2) - (x(3)/r3) + \\
(2*x(2)*(1-x(1))*(A12*x(1)) + (A21*x(2))) - (A21*(x(2)^2)) + (2*x(3)*(1-x(1))*(A13*x(1)) + (A31*x(3)))) - (A31*(x(3)^2)) - (2*x(3)*x(2)*((A23*x(2)) + (A32*x(3))))) + (C*x(2)*x(3)*(1-(2*x(1)))); \\
F(2) = x(2);
F(3) = 1-x(1)-x(2)-x(3);
end