June 2019

Sorption of Benzene, Toluene and Ethylbenzene by Plasticized PEMA and PEMA/PMMA Sensing Films Using a Quartz Crystal Microbalance (QCM) at 298.15K

Deekshitha Adapa
University of South Florida, deekshithaa@mail.usf.edu

Follow this and additional works at: https://scholarcommons.usf.edu/etd

Part of the Chemical Engineering Commons

Scholar Commons Citation
Adapa, Deekshitha, "Sorption of Benzene, Toluene and Ethylbenzene by Plasticized PEMA and PEMA/PMMA Sensing Films Using a Quartz Crystal Microbalance (QCM) at 298.15K" (2019). Graduate Theses and Dissertations.
https://scholarcommons.usf.edu/etd/7720

This Thesis is brought to you for free and open access by the Graduate School at Scholar Commons. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact scholarcommons@usf.edu.
Sorption of Benzene, Toluene and Ethylbenzene by Plasticized PEMA and PEMA/PMMA Sensing Films Using a Quartz Crystal Microbalance (QCM) at 298.15K

by

Deekshitha Adapa

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

Co-Major Professor: Venkat Bhethanabotla, Ph.D.
Co-Major Professor: Scott Campbell, Ph.D.
John Kuhn, Ph.D.

Date of Approval:
June 11, 2019

Keywords: thermodynamics, sorption, plasticizer, copolymer

Copyright © 2019, Deekshitha Adapa
DEDICATION

This thesis is dedicated to my parents for their constant support and motivation.
ACKNOWLEDGEMENTS

I would like to express my gratitude to Dr. Venkat Bhethanabotla and Dr. Scott Campbell for their constant support and help throughout the period of the thesis. I would like to thank Abhijeet Iyer and Jonathan Samuelson for their timely encouragement and technical support. The weekly meetings and some valuable discussions helped me in my successful completion of my thesis. I thank my family for their unconditional trust and endless patience which kept me going all along.
# TABLE OF CONTENTS

List of Tables ........................................................................................................................... ii

List of Figures ........................................................................................................................... iii

Abstract .................................................................................................................................. vi

Chapter 1: Introduction ............................................................................................................ 1
  1.1 Motivation ......................................................................................................................... 1
  1.2 Piezoelectric Effect .......................................................................................................... 2
  1.3 Quartz Crystal Microbalance (QCM) .............................................................................. 2
  1.4 Plasticization .................................................................................................................... 4
  1.5 Previous Work .................................................................................................................. 5
  1.6 Thesis Outline .................................................................................................................. 6

Chapter 2: Thermodynamics .................................................................................................... 7
  2.1 Introduction ...................................................................................................................... 7
  2.2 Vapor-Liquid Equilibrium .............................................................................................. 7
  2.3 Flory-Huggins Model ..................................................................................................... 10

Chapter 3: Experimental Apparatus ......................................................................................... 14
  3.1 Materials ......................................................................................................................... 14
  3.2 Apparatus Design .......................................................................................................... 17
  3.3 Procedure ....................................................................................................................... 18

Chapter 4: Results and Discussion .......................................................................................... 21

Chapter 5: Conclusion and Future Work .................................................................................. 39
  5.1 Conclusion ....................................................................................................................... 39
  5.2 Future Work .................................................................................................................... 39

References ............................................................................................................................... 40

Appendix A: Additional Information ......................................................................................... 43
**LIST OF TABLES**

Table 1: Antoine parameters for benzene, toluene and ethylbenzene .................................................. 10

Table 2: Molar volume, molar mass and Hansen solubility parameters of solvents ................................. 12

Table 3: Molar volume, molar mass and Hansen solubility parameters of polymers and plasticizers .......................................................................................................................... 13

Table 4: Structures of PEMA and PMMA .................................................................................................. 14

Table 5: Structures of plasticizers DBP, DBS and BS .............................................................................. 15

Table 6: Activity as a function of weight fraction data for sorption of benzene in pure PEMA and plasticized PEMA .................................................................................................................. 23

Table 7: Activity as a function of weight fraction data for sorption of toluene in pure PEMA and plasticized PEMA .................................................................................................................. 24

Table 8: Activity as a function of weight fraction data for sorption of ethylbenzene in pure PEMA and plasticized PEMA .................................................................................................................. 25

Table 9: Activity as a function of weight fraction data for sorption of benzene in pure PEMA/PMMA copolymer and plasticized copolymer .................................................................................................................. 29

Table 10: Activity as a function of weight fraction data for sorption of toluene in pure PEMA/PMMA copolymer and plasticized copolymer .................................................................................................................. 30

Table 11: Activity as a function of weight fraction data for sorption of ethylbenzene in pure PEMA/PMMA copolymer and plasticized copolymer .................................................................................................................. 31

Table 12: Interaction parameters after Flory-Huggins modelling along with the adjustable parameter used in each solvent for PEMA .................................................................................................................. 35

Table 13: Interaction parameters after Flory-Huggins modelling along with the adjustable parameter used in each solvent for PEMA/PMMA copolymer .................................................................................................................. 36

Table 14: Partition coefficients at infinite dilution of PEMA and plasticized PEMA .............................................. 37

Table 15: Partition coefficients at infinite dilution of copolymer and plasticized copolymer ................................. 38
LIST OF FIGURES

Figure 1: Equivalent circuit for Butterworth-Van Dyke (BVD) model ........................................... 3
Figure 2: AT and BT cut quartz crystals ......................................................................................... 16
Figure 3: Model QCM ....................................................................................................................... 16
Figure 4: 5 MHz Quartz crystal ......................................................................................................... 17
Figure 5: Schematic diagram of the flow system .............................................................................. 17
Figure 6: Spin coater ......................................................................................................................... 19
Figure 7: Experimental vs literature data comparison of poly (isobutylene) ..................................... 21
Figure 8: Frequency time plot for the sorption of ethylbenzene in pure PEMA .............................. 22
Figure 9: Frequency time plot for the sorption of ethylbenzene in PEMA with 17.5% of DBP ....... 22
Figure 10: Activity as a function of weight fraction curves of benzene in PEMA and plasticized PEMA ................................................................. 26
Figure 11: Activity as a function of weight fraction curves of toluene in PEMA and plasticized PEMA ......................................................................................... 27
Figure 12: Activity as a function of weight fraction curves of ethylbenzene in PEMA and plasticized PEMA ......................................................................................... 28
Figure 13: Activity as a function of weight fraction curves of benzene in PEMA/PMMA copolymer and plasticized copolymer ........................................................................... 32
Figure 14: Activity as a function of weight fraction curves of toluene in PEMA/PMMA copolymer and plasticized copolymer ........................................................................... 33
Figure 15: Activity as a function of weight fraction curves of ethylbenzene in PEMA/PMMA copolymer and plasticized copolymer ........................................................................... 34
Figure a1: Comparison of model vs experimental data of benzene in pure PEMA ....................... 43
Figure a2: Comparison of model vs experimental data of toluene in pure PEMA .......................... 44
Figure a3: Comparison of model vs experimental data of ethylbenzene in pure PEMA ............... 45
Figure a4: Comparison of model vs experimental data of benzene in pure PEMA/PMMA copolymer ................................................................. 46

Figure a5: Comparison of model vs experimental data of toluene in pure PEMA/PMMA copolymer ........................................................................ 47

Figure a6: Comparison of model vs experimental data of ethylbenzene in pure PEMA/PMMA copolymer .................................................................. 48

Figure a7: Comparison of model vs experimental data of benzene in PEMA with 17.5% DBP ......... 49

Figure a8: Comparison of model vs experimental data of toluene in PEMA with 17.5% DBP ........... 50

Figure a9: Comparison of model vs experimental data of ethylbenzene in PEMA with 17.5% DBP ........................................................................................................ 51

Figure a10: Comparison of model vs experimental data of benzene in PEMA with 17.5% DBS .......... 52

Figure a11: Comparison of model vs experimental data of toluene in PEMA with 17.5% DBS .......... 53

Figure a12: Comparison of model vs experimental data of ethylbenzene in PEMA with 17.5% DBS .................................................................................................................. 54

Figure a13: Comparison of model vs experimental data of benzene in PEMA with 17.5% BS ........... 55

Figure a14: Comparison of model vs experimental data of toluene in PEMA with 17.5% BS .......... 56

Figure a15: Comparison of model vs experimental data of ethylbenzene in PEMA with 17.5% BS .......................................................................................................................... 57

Figure a16: Comparison of model vs experimental data of benzene in PEMA/PMMA copolymer with 17.5% DBP .................................................................................................... 58

Figure a17: Comparison of model vs experimental data of toluene in PEMA/PMMA copolymer with 17.5% DBP ................................................................................................. 59

Figure a18: Comparison of model vs experimental data of ethylbenzene in PEMA/PMMA copolymer with 17.5% DBP ................................................................................................. 60

Figure a19: Comparison of model vs experimental data of benzene in PEMA/PMMA copolymer with 17.5% DBS .................................................................................................... 61

Figure a20: Comparison of model vs experimental data of toluene in PEMA/PMMA copolymer with 17.5% DBS .................................................................................................... 62

Figure a21: Comparison of model vs experimental data of ethylbenzene in PEMA/PMMA copolymer with 17.5% DBS .................................................................................................... 63

Figure a22: Comparison of model vs experimental data of benzene in PEMA/PMMA copolymer with 17.5% BS .................................................................................................... 64
Figure a23: Comparison of model vs experimental data of toluene in PEMA/PMMA copolymer with 17.5% BS............................................................................................................. 65

Figure a24: Comparison of model vs experimental data of ethylbenzene in PEMA/PMMA copolymer with 17.5% BS........................................................................................................................................ 66
ABSTRACT

Detection of volatile organic compounds (VOC’s) in the environment is important for human health and wellness. Long term exposure of certain VOC’s like benzene, toluene, ethylbenzene and xylene (BTEX) has a severe effect on human health. There are techniques such as gas chromatography, photo ionization, and mass spectroscopy that are time consuming, require gas sampling and are ineffective in real time sensing in air. Acoustic wave devices such as surface acoustic wave (SAW) devices can be used for sensing BTEX compounds in both vapor and liquid phase. The quartz crystal microbalance (QCM) is a low-frequency acoustic wave device, which can be used to characterize polymer film sensing quickly and easily by studying the sorption properties of BTEX compounds in them. In this work, thin films (~ 0.5 microns) of polymer/plasticizer blends are spin-coated on a 5MHz QCM for the detection of VOC’s. A polymer/plasticizer combination of poly (ethyl methacrylate) (PEMA) and a copolymer of poly (ethyl methacrylate) and poly (methyl methacrylate) (PEMA/PMMA) with di n-butyl phthalate (DBP), di-n-butyl sebacate (DBS) and n-butyl stearate (BS) are used for the detection of benzene, toluene and ethylbenzene in vapor phase. The working apparatus consists of a stream of solvent vapor diluted with nitrogen to an arbitrary concentration passing over the QCM oscillated to its resonant frequency. The sorption data are reported at 298.15 K in terms of activity as a function of weight fraction curves and are interpreted with the Flory-Huggins ternary model. The addition of plasticizer modifies the free volume properties of the polymer, thereby increasing diffusion and sensitivity of BTEX vapors. The plasticizer composition is tailored to 17.5%, for maximum sorption with minimal viscoelastic effects. The sorption and sensitivity of BTEX are interpreted and studied in terms of plasticizer type and concentration.
CHAPTER 1: INTRODUCTION

1.1 Motivation

There is an increase in demand for the detection and measurement of chemical species in the environment. VOCs are organic chemicals present in indoor air, which are emitted from a large number of indoor sources like consumer products, furnishings, building materials, tobacco smoking, etc. They easily vaporize at room temperature and pressure. Outdoor air is also a source of indoor VOCs. Some of the most common indoor VOC’s are benzene, toluene, ethylbenzene, and xylene (BTEX) are present at very low concentrations but are important due to their significant health hazard due to toxicity.

To circumvent the shortcomings of current sensor systems, modern techniques are being employed to improve the selectivity, sensitivity and minimize the limitations in measurement of vapor sorption. Surface acoustic wave (SAW) devices are used as chemical sensors for the detection of change of mass on the surface in terms of frequency changes. 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. Quartz crystal microbalance (QCM) is a SAW sensor that offers high sensitivity with less equilibration times. The amount of sorption depends upon the physical and chemical properties of the film coated on the QCM. Sorption of benzene, toluene and ethylbenzene in different polymer/plasticizer blends is important for the interpretation of the effect of plasticizer on a polymer. Plasticizers of different molecular sizes and structures are explored for better sensitivity of sensors.
1.2 Piezoelectric Effect

Many sensors and actuators work on the principle of the piezoelectric effect. Cady defines piezoelectricity as, “the electrical polarization produced by mechanical strain in crystals”\(^1\). It is the accumulation of charges inside a crystalline material when an external mechanical or electrical force is implied. A material needs to have an isotropic polycrystalline structure in order to exhibit piezoelectric property. Piezoelectricity can also be induced by a temporary application of a strong electric field. A good chemical sensor allows the transduction of chemical or physical properties at the interface. It should be able to provide electrical information as a function of a chemical identity or change in concentration\(^1\). The acoustic wave sensors trigger acoustic waves electrically at the input transducer and receive it at the output transducer\(^3\). In our experiments, we use an AT-cut piezoelectric quartz crystal in a quartz crystal microbalance to generate acoustic waves to study the sorption of solvents in plasticized polymers.

1.3 Quartz Crystal Microbalance (QCM)

A quartz crystal microbalance (QCM) is used to measure the change in frequency per unit area variation in mass of a quartz crystal resonator. QCM resonators have a wide range of uses because of their cost-effectiveness, stability, precision and small size. A QCM is highly repeatable with respect to data and is stable with respect to properties such as temperature, time and environmental changes. An AT-cut quartz crystal is used in this thesis, where the quartz blank is cut at an angle of 33°15’ to the optical axis of the crystal. A linear relationship between frequency shift (\(\Delta f\)) and mass change of the crystal is given by Saurbrey equation\(^4\).

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

\[
\Delta f = -C_1 \Delta m
\]

where, \(\Delta f\) – Frequency shift

\(f\) – Intrinsic frequency of the crystal
\( \rho_q \) – Density of the quartz crystal

\( \mu \) – Shear modulus

A – Piezoelectrically active crystal area

\( \Delta m \) – Change in mass/ area of crystal

\( C_f \) – Sensitivity factor

The Saurbrey equation is valid only for small mass loadings and for vapor sensing applications only. Change in the mass of film results in frequency shifts, which depends on the selectivity and sensitivity of the film. A thin uniform film is important in gas phase detection in order to obey Saurbrey’s equation. In the case of thick films, an equivalent circuit model is used to study the changes in electrical properties of the system and for the calculation of losses induced due to thick films. In this work, a 5 MHz quartz crystal is used for gas-phase mass detection of organic compounds at room temperature.

An equivalent circuit model called the Butterworth-Van Dyke (BVD) model is used to provide the electrical characteristics of a quartz crystal microbalance coated with a polymer film.

![Figure 1: Equivalent circuit for Butterworth-Van Dyke (BVD) model](https://doi.org/10.1016/j.snb.2006.07.016)


where, \( C_0 \) - parallel capacitance

\( C_1 \) - motional capacitance

\( L_1 \) - motional inductance

\( R_1 \) - motional resistance

Figure 1 is modified and referred to High Frequency Thickness Shear Mode Devices for Organic Vapor Sensing by R.Williamsand and A.K.Upadhyayula. The electrical equivalents of inertia, stiffness and
internal losses of the mechanically vibrating system are given by $L_1$, $C_1$, $R_1$. But, $C_0$ is the static capacitance present between the electrodes across the quartz crystal. These electrical properties are related to the actual physical properties of the QCM as well as the surface loadings by the following equations$^5$,

$$C_0 = \frac{\varepsilon_{22} A}{h_s}$$  \hspace{1cm} (3)

$$C_1 = \frac{8K^2C_0}{(N\pi)^2}$$  \hspace{1cm} (4)

$$L_1 = \frac{1}{\omega_s^2 C_1}$$  \hspace{1cm} (5)

$$R_1 = \frac{\eta_q}{\mu_q C_1}$$  \hspace{1cm} (6)

where, $h_s$ - electrode area

$\omega_s$ - series resonant frequency

$K^2$ - quartz electromechanical coupling coefficient

$\varepsilon_{22}$ - dielectric permittivity

$\mu_q, \rho_q, \eta_q$ - shear stiffness, mass density and effective viscosity of quartz crystal

1.4 Plasticization

Plasticizers play a vital role in the polymer industry, due to their effect on polymer properties. Currently, in industry, plasticizers are used for various purposes like viscosity control, reducing glass transition temperature, softening, modification of adhesion properties, etc. in products like paints, tires, roofing materials and more$^6$. Various theories like the gel theory, lubrication theory, and viscosity theory explain the plasticization action of plasticizers in polymer/plasticizer blends. Classically, the first two theories that explained the concept of plasticization are the gel and lubrication theory. The lubrication theory explains the reduction of friction between different polymer molecules allowing easier slipping action. Whereas the gel theory explains the plasticization action due to the deformation of polymer molecules without breaking resulting in reduced rigidity of polymer molecules. In gel theory, the polymer
molecules are considered to have a tridimensional honeycomb structures attached by weak bonds, due to which they possess aggregation-deaggregation equilibria between the polymer molecules. These two theories failed to explain some properties like thermal expansion, specific volumes or viscosity with respect to temperature, which was later explained by the free volume theory. Free volume theory explains the effect of polymer structure, molecular weight, terminal groups, presence of plasticizer or a different monomer on the polymer properties. Glass transition temperature is another property that is affected due to the addition of a plasticizer. Glass transition temperature corresponds to the temperature at which polymers change from glassy to a rubbery polymer. Polymeric materials with same free volume show similar glass transition temperatures. Initially, Fox and Flory explained the free volume of glasses to be zero for any temperature below the glass transition temperature. Later, Kanig explained free volume as the difference between the measured free volume at that temperature and the observed free volume at absolute zero temperature.

\[ v_f = v_T - v_0 \]  

This theory didn’t hold due to the difficulty in the measurement of free volume at absolute zero temperature. Sears and Darby stated that motion of a polymer chain increases with an increase in free volume. The three main sources for free volume are motion of chain ends, side chains, and the main chain. The addition of plasticizer effected these sources resulting in an increase in free volume, resulting in a decrease of the glass transition temperature. It is also observed that branched plasticizers with large molecular sizes increase the free volume of the polymeric material.

Selection of right polymer/plasticizer combination plays an important role in the extent of plasticization action, for better sorption. This usually involves a compromise on compatibility, efficiency or solvent power.

**1.5 Previous Work**

Sorption of organic solvents like benzene, toluene and ethylbenzene is observed in both vapor and liquid phase. Polymers like poly (ethyl methacrylate), poly (methyl methacrylate), poly (isobutylene) and
poly (styrene) with solubility parameters close to that of benzene, toluene and ethylbenzene are chosen. Josse has reported the detection of benzene in water at a concentration less than 100 ppb using a plasticized polymer coating on a shear horizontal surface acoustic wave device (SH-SAW) sensor. This work was later continued using plasticized poly (methyl methacrylate) for the detection of various hydrocarbons in water. In our group, Wong reported the sorption of organic vapors like benzene using poly (ethyl methacrylate), poly (methyl methacrylate) and their copolymers at 323.15 K. The experimental setup was later modified by Samuelson and Iyer, who reported the sorption data for benzene using poly (ethylene glycol) and poly (caprolactone) at 298.15 K. Utilizing thicker films on the QCM which show viscoelasticity, Richardson extracted the viscoelastic modulus of poly (isobutylene) at different cell temperatures and at different sorption weight fractions.

1.6 Thesis Outline

Within context of this previous work, my thesis concentrates on the sorption of benzene, toluene and ethylbenzene using poly (ethyl methacrylate) and a copolymer of poly (methyl methacrylate) and poly (ethyl methacrylate) with 17.5% of plasticizers like di n-butyl phthalate, di n-butyl sebacate and n-butyl stearate at 298.15 K. This thesis is organized into 5 chapters. Chapter 1 explains my interest in choosing this project with some fundamental backgrounds. Chapter 2 deals with the thermodynamics part of the project and explains the theory behind vapor-liquid equilibrium, Flory Huggins modelling, and viscoelasticity. Chapter 3 gives a complete description of the apparatus being used and the procedure utilized for the sorption of organic vapors. After this, sorption data along with the Flory Huggins modelling of these data are reported along with the activity-weight fraction plots for better comparison. Discussion has been made on how the chemical and structural properties of the plasticizers affect sorption. Chapter 5 gives a conclusion for the thesis work followed with some prospective continuations of research in this area.
CHAPTER 2: THERMODYNAMICS

2.1 Introduction

The Hansen solubility parameters explain the solubility of solvents in polymers or plasticized polymers. A mathematical model for the solubility of solvents in polymer/plasticizer blends is developed by data correlation. The experimental activity-weight fraction data is fit to modelled weight fraction data to obtain the correlated data. In this work, a methodology is presented where Hansen solubility parameters are utilized in Flory-Huggins model which helps predict solubilities of solvents in different polymer/plasticizer blends. 15

2.2 Vapor-Liquid Equilibrium

In order to reach equilibrium, the fugacity of the solvent in liquid phase must be equal to the fugacity of solvent in the vapor phase16.

\[ f_{1\text{,vapor}} = f_{1\text{,liquid}} \]  

(8)

The fugacity and the activity coefficients of solvent in vapor and liquid phase are equated as follows,

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

(9)

where, \( \phi_1 \) - fugacity coefficient
\( \gamma_1 \) - activity coefficient
\( y_1 \) - mole fraction of solvent in vapor phase coming in contact with the polymer/plasticizer film
\( x_1 \) - mole fraction of solvent in liquid phase by considering the solvent solution is pure
\( f_{1\text{,pure}} \) - fugacity of pure solvent
According to the concept of partial pressures,

\[ y_1 P = P_1 \]  \hspace{1cm} (10)

For a two-component gas phase system, the fugacity of one of the components is written as,

\[ \phi_1 = \exp\left(\frac{P}{RT} (B_{11} + y_3^2(2B_{13} - B_{11} - B_{33}))\right) \]  \hspace{1cm} (11)

where, \( B_{11}, B_{13}, B_{33} \) - second virial coefficients

\( R \) - universal gas constant

\( P \) - total pressure

\( T \) - temperature of the system

The correlation for the calculation of the second virial coefficient at the temperature of the system was proposed by Tsonopolus,

\[ B_{11} = \frac{RT_c}{P_c} (f^{(0)}(T_R) + \omega f^{(1)}(T_R)) \]  \hspace{1cm} (12)

where, \( T_c \) - critical temperature

\( P_c \) - critical pressure

\( \omega \) - Pitzer’s accentric factor

\( T_R \) - reduced temperature

\[ f^{(0)}(T_R) = 0.1445 - \frac{0.330}{T_R} - \frac{0.1358}{T_R^2} - \frac{0.0121}{T_R^3} \]  \hspace{1cm} (13)

\[ f^{(1)}(T_R) = 0.073 - \frac{0.46}{T_R} - \frac{0.5}{T_R^2} - \frac{0.097}{T_R^3} - \frac{0.0073}{T_R^4} \]  \hspace{1cm} (14)

For liquid phase,

\[ f^l_{1 \text{ pure}} = x_1 y_1 f^l_1 \]  \hspace{1cm} (15)

\[ f^l_1 = P_1 \text{ sat} \phi_1 \text{ sat} \exp \left( \frac{v_1 \text{ sat}}{RT} \left( P - P_1 \text{ sat} \right) \right) \]  \hspace{1cm} (16)

\[ f^l_1 = P_1 \text{ sat} \exp \left( \frac{B_{11} P_1 \text{ sat}}{RT} \right) \exp \left( \frac{v_1 \text{ sat}}{RT} \left( P - P_1 \text{ sat} \right) \right) \]  \hspace{1cm} (17)
At vapor-liquid equilibrium,

\[ P_1 \exp \left( \frac{P}{RT} (B_{11} + y_3^2 (2B_{13} - B_{11} - B_{33})) \right) = x_1 y_1 P_1^{\text{sat}} \exp \left( \frac{B_{11} P_1^{\text{sat}}}{RT} \right) \exp \left( \frac{v_1^{\text{sat}}}{RT} (p - P_1^{\text{sat}}) \right) \]  

(18)

After rearranging the expression\(^\text{14}\),

\[ x_1 y_1 = \omega_1 \Omega_1 = a_1 = \frac{y_1 P_1 \exp \left( \frac{P}{RT} (B_{11} + y_3^2 (2B_{13} - B_{11} - B_{33})) \right)}{P_1^{\text{sat}} \exp \left( \frac{B_{11} P_1^{\text{sat}}}{RT} \right) \exp \left( \frac{v_1^{\text{sat}}}{RT} (p - P_1^{\text{sat}}) \right)} \]  

(19)

\[ a_1 = \frac{y_3 P_1}{P_1^{\text{sat}}} \exp \left( \frac{P_1 - P_1^{\text{sat}}}{RT} B_{11} + \frac{P_1 (1 - y_1)^2 (2B_{13} - B_{11} - B_{33})}{RT} \right) \]  

(20)

Considering, \( x_1 = 1 \) and \( y_1 = 1 \), the mole fraction of solvent leaving the impinger is

\[ y_{1B} = \frac{P_1^{\text{sat}}}{P_1} \left( \frac{1}{\exp \left( \frac{P_1 - P_1^{\text{sat}}}{RT} B_{11} + \frac{P_1 (1 - y_1)^2 (2B_{13} - B_{11} - B_{33})}{RT} \right)} \right) \]  

(21)

The mole fraction \( y_1 \) is obtained from the mass balance at the point of mixture of solvent from bubbler with the diluent flow.

\[ y_1 = \frac{y_{1B} V_{31}}{V_{31} + (1 - y_{1B}) V_{32}} \]  

(22)

where, \( V_{31}, V_{32} \) - volumetric flowrates of nitrogen through both the mass flow controllers.

The equation is solved at the temperature of the impingers (\( T' \)) and the pressure (\( P \)) in the impingers. Saturated vapor pressure at the temperature of the cell (\( T \)) and temperature of the impingers (\( T' \)) can be calculated using Antoine equation.

\[ \ln(P_1^{\text{sat}}) = A - \frac{B}{T' + C} \]  

(23)
Table 1: Antoine parameters for benzene, toluene and ethylbenzene

<table>
<thead>
<tr>
<th>Antoine parameters</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>(bar K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>4.01814</td>
<td>4.07</td>
<td>4.0825</td>
</tr>
<tr>
<td>B</td>
<td>1203.835</td>
<td>1419.31</td>
<td>1346.4</td>
</tr>
<tr>
<td>C</td>
<td>-53.226</td>
<td>-60.54</td>
<td>-53.1</td>
</tr>
</tbody>
</table>

Note: Adapted from Kaur, K. Sorption of Benzene, Toluene and Ethylbenzene by Plasticized Poly (Ethyl Methacrylate) Using Quartz Crystal Microbalance at 298.15K; 2018.

2.3 Flory-Huggins Model

The sorption data is correlated by fitting experimental data to Flory-Huggins model using activity as a function of weight fraction curves.

\[
\frac{N G^E}{RT} = N_1 \ln \phi_1 + N_2 \ln \frac{\phi_2}{x_2} + \chi \phi_1 \phi_2 (N_1 + rN_2) \quad (24)
\]

where, \( x_1, x_2 \) - mole fractions of solvent and polymer
\( \phi_1, \phi_2 \) - volume fractions of solvent and polymer
\( r = \frac{V_2}{V_1} \) - ratio of molar volumes
\( N_1, N_2 \) - number of moles of solvent and polymer
\( \chi \) - adjustable parameter

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

\[
\ln a_s = \ln \phi_s + \left(1 - \frac{V_s}{V_p}\right) \phi_p + \chi \phi_p^2 \quad (25)
\]

where, \( a_s \) - activity of solvent
\( \phi_s, \phi_p \) - volume fraction of solvent and polymer
\( \chi \) - polymer-solvent interaction parameter and were obtained by minimizing the sum of squares between calculated and model activities

\( V_s, V_p \) - molar volume of solvent and polymer

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

\[
\phi_s = \frac{V_s x_s}{V_{sx_s} + V_{px_p}} \tag{26}
\]

\[
\phi_p = \frac{V_p x_p}{V_{px_p} + V_{px_p}} \tag{27}
\]

where, \( x_s, x_p \) - mole fractions of solvent and polymer

The equation\(^{15}\) for a binary system can be extended to a ternary system of a polymer (p) and two solvents (s\(_1\) and s\(_2\)) which turns out to be a non-linear equation system as follows,

\[
\ln a_{s_1} = \ln \phi_{s_1} + (1 - \phi_{s_1}) - \left( \frac{V_{s_1}}{V_{s_2}} \right) \phi_{s_2} - \left( \frac{V_{s_1}}{V_p} \right) \phi_p + \left( \chi_{s_1 s_2} \phi_{s_2} + \chi_{s_1 p} \phi_p \right)(\phi_{s_2} + \phi_p) - \chi_{s_2 p} \left( \frac{V_s}{V_{s_2}} \right) \phi_{s_2} \phi_p \tag{28}
\]

Similar equations can be written for the polymer and the other solvent. To solve the above equation, we require the information regarding the molar volumes, volume fractions and interaction parameters of all three entities in the considered system.

A binary interaction parameter can be expressed in terms of Hansen solubility parameters as,

\[
\chi_{12} = \alpha \frac{V_s}{RT} \left( (\delta_{i,d} - \delta_{j,d})^2 + 0.25(\delta_{i,p} - \delta_{j,p})^2 + 0.25(\delta_{i,h} - \delta_{j,h})^2 \right) \tag{29}
\]

The interaction parameters are calculated for each system by having an adjustable parameter (\( \alpha \)). Each system consists of sorption data of each solvent (benzene, toluene and ethylbenzene) in pure polymer and plasticized polymers. The squared errors of the activities for each solvent system are added and are minimized by varying \( \alpha \). The value of \( \alpha \) ranges from 0 to 1 for each solvent system. This provides us with 3 different \( \alpha \) for each system benzene, toluene and ethylbenzene respectively. The Hansen solubility parameters, the molar volume, and molar mass data are provided in the following table.
Table 2: Molar volume, molar mass and Hansen solubility parameters of solvents

<table>
<thead>
<tr>
<th>Component</th>
<th>Molar mass (M, g/mol)</th>
<th>Molar volume (V, ml/mol)</th>
<th>δ_d</th>
<th>δ_p</th>
<th>δ_h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>78.11</td>
<td>89.17</td>
<td>18.4</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>92.14</td>
<td>105.91</td>
<td>18.0</td>
<td>1.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>106.97</td>
<td>123.52</td>
<td>17.8</td>
<td>0.6</td>
<td>1.4</td>
</tr>
</tbody>
</table>

*Note: Adapted from Hansen, C. M. *Hansen Solubility Parameters - A User’s Handbook*; CRC Press*
Table 3: Molar volume, molar mass and Hansen solubility parameters of polymers and plasticizers

<table>
<thead>
<tr>
<th>Component</th>
<th>Component</th>
<th>Molar mass ($M_i$, g/mol)</th>
<th>Molar volume ($V_i$, ml/mol)</th>
<th>$\delta_d$</th>
<th>$\delta_p$</th>
<th>$\delta_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (ethyl methacrylate)</td>
<td>PEMA</td>
<td>340000</td>
<td>306306.30</td>
<td>17.5</td>
<td>1.3</td>
<td>7.1</td>
</tr>
<tr>
<td>Copolymer of poly (ethyl methacrylate) and poly (methyl methacrylate)</td>
<td>PEMA/PMMA</td>
<td>250000</td>
<td>221000</td>
<td>17.8</td>
<td>4.1</td>
<td>7.2</td>
</tr>
<tr>
<td>di n-butyl phthalate (DBP)</td>
<td></td>
<td>278.34</td>
<td>265.09</td>
<td>17.8</td>
<td>8.6</td>
<td>4.1</td>
</tr>
<tr>
<td>di n-butyl sebacate (DBS)</td>
<td></td>
<td>314.47</td>
<td>339.01</td>
<td>16.7</td>
<td>4.5</td>
<td>4.1</td>
</tr>
<tr>
<td>n-butyl stearate (BS)</td>
<td></td>
<td>340.59</td>
<td>382</td>
<td>14.5</td>
<td>3.7</td>
<td>3.5</td>
</tr>
</tbody>
</table>

CHAPTER 3: EXPERIMENTAL APPARATUS

3.1 Materials

Solvents benzene, ethylbenzene, and toluene with 99% purity were purchased from Sigma Aldrich and are used as is. Poly (ethyl methacrylate) (PEMA) with a molecular mass of 340000 g/mol was purchased from Sigma – Aldrich, and a copolymer of poly (methyl methacrylate-ethyl methacrylate) with a calculated 250000 g/mol was purchased from Polysciences Inc. Plasticizers di n-butyl phthalate (DBP) (MW 278.34), di n-butyl sebacate (DBS) (MW 314.47), n-butyl stearate (BS) (MW 340.59) were purchased from Scientific Polymer Products, Inc.

Table 4: Structures of PEMA and PMMA

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (ethyl methacrylate) (PEMA)</td>
<td><img src="image" alt="Structure of PEMA" /></td>
</tr>
<tr>
<td>Poly (methyl methacrylate) (PMMA)</td>
<td><img src="image" alt="Structure of PMMA" /></td>
</tr>
</tbody>
</table>

*Note: Adapted from Hansen, C. M. Hansen Solubility Parameters - A User’s Handbook; CRC Press*
### Table 5: Structures of plasticizers DBP, DBS and BS

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di n-butyl phthalate (DBP)</td>
<td><img src="image1" alt="Structure of DBP" /></td>
</tr>
<tr>
<td>Di n-butyl sebacate (DBS)</td>
<td><img src="image2" alt="Structure of DBS" /></td>
</tr>
<tr>
<td>n-butyl stearate (BS)</td>
<td><img src="image3" alt="Structure of BS" /></td>
</tr>
</tbody>
</table>

*Note: Adapted from Hansen, C. M. Hansen Solubility Parameters - A User’s Handbook; CRC Press*

The effect of added mass on the resonant frequency of material is explored using a quartz crystal resonator. High-frequency thickness shear mode is a mode of vibration which is most sensitive for the detection of addition or removal of mass of a quartz crystal resonator. For the detection of weight in very minute quantities, the plate should be cut only in specific orientations with respect to the central axes. Figure 2 shows the cuts and their orientation with respect to central axis, it is referred to thesis report by Anath K Upadhyula\(^5\). A periodic voltage is applied to the quartz crystal across the thin metal electrodes wrapped around the crystal to vibrate to the frequency of the applied voltage. Resonant frequency can be achieved
by using a feedback network of a closed loop system with an amplifier, which can be obtained when the applied voltage is close to the mechanical resonant frequency of the crystal\(^5\).

![Figure 2: AT and BT cut quartz crystals](image)


The working model of a quartz crystal microbalance is explained in fig. 3 where at resonance the wavelength is equal to half of the quartz crystal thickness and resonant frequency decreases with an increase in the crystal thickness. It is also to be noted that the equivalent mass is calculated considering the mass deposited on the quartz crystal.

![Figure 3: Model QCM](image)

In this project, a 5 MHz AT-cut quartz crystal is used. A gold electrode is wrapped around a quartz crystal for allowing electrical contact on one side. Quartz crystal with a diameter of 1 inch and 0.013-inch
thickness are used and are polished on both sides to have good stability and high sensitivity. The operating frequency is 5 MHz with a resistance ranging from 6-10 ohm.

![Figure 4: 5 MHz Quartz crystal](image)

3.2 Apparatus Design

![Figure 5: Schematic diagram of the flow system](image)


Figure 5 is drawn by referring to Sorption of Benzene, Dichloroethane, Dichloromethane, and Chloroform by Poly(Ethylene Glycol), Polycaprolactone, and Their Copolymers at 298.15 K Using a Quartz Crystal Microbalance by A. R Iyer and J. J Samuelson. The vapor flow is supported by using nitrogen as the carrier gas. Ultra-high pure (UHP) nitrogen is provided by Airgas and is used at a pressure range of 40-50 psig. The flow of nitrogen to the cell and impingers are regulated using two 100 sccm mass flow...
controllers provided by MKS. The direction of flow is regulated using normally closed Teflon valves both at the inlet and outlet of the impingers. The impingers and the QCM cell are maintained at 288K and 298K respectively, by flowing water continuously which are maintained using water baths.

The QCM cell is designed in such a way it holds the crystal with the help of O-rings on both the sides of the cell. The cell has two pogo pins on the bottom side such that they touch both the electrode surfaces to apply and measure voltage differences and frequencies. The cell also has two openings for the solvent mixture to flow onto the crystal surface for sorption and the other outlet for the vapors to leave the cell. The cell is jacketed for water to flow continuously in order to maintain the cell temperature at room temperature (298 K). A phase lock oscillator which is tuned to the resonant frequency of the cell is used to make sure that the quartz crystal is placed in lock position inside the QCM cell. A frequency counter is used to measure the frequency of crystal during the sorption of the solvent vapors. This signal is sent to the computer which is interfaced using a GPIB cable and is recorded using LabVIEW software.

3.3 Procedure

1. Preparation of polymer/plasticizer blend:

   Hansen solubility parameters are used for the prediction of polymers in solvents. The equation 27 developed by Skaarup for the calculation of solubility parameter distance, Ra, using solubility parameters with the subscripts d, p, h representing dispersion, dipolar intramolecular and hydrogen bonding forces respectively.

   \[ Ra^2 = 4(\delta_D^2 - \delta_D^1)^2 + (\delta_P^2 - \delta_P^1)^2 + (\delta_H^2 - \delta_H^1)^2 \]  (30)

   For good solubility or high affinity, it requires Ra to be less than Ro. The relative energy difference is represented using the RED number which is the ratio of Ra to Ro.

   \[ RED = \frac{Ra}{Ro} \]  (31)

   where,

   Ra – distance between Hansen solubility parameters
Ro – radius of sphere in Hansen space

The RED number value indicated the following:

RED = 0, no energy difference
RED < 1, high affinity
RED = 1, boundary condition
High RED, lower affinities.

In this project, chloroform is chosen as the solvent to dissolve polymer/plasticizers. A pure solution of polymer or copolymer is prepared by adding 0.25g in 10ml of chloroform. For the preparation of 17.5% polymer/plasticizer blend. We add 0.206g of polymer and the respective volume of plasticizer which calculated using the density of plasticizer, to a 10ml of chloroform solution. This mixture is allowed to sonicate for 20-30 minutes and is spin-coated on to a crystal using a Spin coater. The thickness of the coating depends on the speed and time of spin-coating.

\[ t \propto \frac{1}{\omega^{3/2}} \]  \hspace{1cm} (32)

Figure 6: Spin coater
In our case, we coated a 300μL solution for an overall period of 5 minutes with speeds of 100rpm, 1000rpm, 5000rpm, 7500rpm and 10000rpm per minute by constantly purging with industrial nitrogen. This process leaves us with a frequency shift of 1500-2500 Hz.

2. Vapor flow and data collection:

The experiment and the data collection are automated using LabVIEW software, where the code is tailored in such a way that the operator can choose the number of data points to be collected, 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 UHP nitrogen gas fed to the mass flow controllers is controlled to produce flows ranging from 0-100sccm with increments in 10sccm summing to a total of 100sccm. The flow is routed using normally closed solenoids present at the inlet and the outlet of the impinger. 10 different isothermal concentrations are produced for all the solvents 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 baths. HP 5334B is used to measure the frequency and is logged to the computer. As the data is being collected, only the last 50 points are stored when the slope of the frequency as a function of time curve is almost 0 or has a confidence of 95%. 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.

3. Cleaning of used crystals:

Used crystals before being spin-coated with the polymer/plasticizer blend are cleaned in a Soxhlet extractor. They are cleaned for 3-4 hours based on the number of crystals being cleaned with chloroform as the circulating solvent at a temperature of 300K. The cleaned crystals are washed using Millipore water and are dried using nitrogen. To make sure the crystal is clean and does not possess any coatings, the frequency and the resistance of the cleaned crystal are measured using a frequency counter.
CHAPTER 4: RESULTS AND DISCUSSION

Data for the sorption of benzene, toluene and ethylbenzene in polymers and plasticized polymers are reported in this section. In order to make sure that the equipment is operating perfectly, sorption of benzene in poly (isobutylene) is compared with literature data\textsuperscript{18}. The following plot shows the comparison of data collected using our equipment vs. literature data at 298K.

![Figure 7: Experimental vs literature data comparison of poly (isobutylene)](image)

The results due to the addition of plasticizer are explained in section 1.3. This increases the free volume thereby increasing the sorption. Figure 9 and 10 show the frequency-time curves for the sorption of ethylbenzene in pure polymer of poly (ethyl methacrylate) and a mixture of poly (ethyl methacrylate) and 17.5% of di n-butyl phthalate at 298K. At each step, a 10sccm of ethylbenzene is added in such a way that the amount of solvent ranges from 10sccm to 100sccm from first to tenth data point. The plots clearly
depict the instantaneous response for sorption in the case of addition of plasticizer, which explains the fact of plasticizer increasing the free volume supports more and faster sorption of solvent vapors.

**Figure 8: Frequency time plot for the sorption of ethylbenzene in pure PEMA**

**Figure 9: Frequency time plot for the sorption of ethylbenzene in PEMA with 17.5% of DBP**
The sorption data of benzene, toluene and ethylbenzene in poly (ethyl methacrylate) with the addition of 17.5% di n-butyl phthalate, di n-butyl sebacate, n-butyl stearate is reported in table 5 to 7.

Table 6: Activity as a function of weight fraction data for sorption of benzene in pure PEMA and plasticized PEMA

<table>
<thead>
<tr>
<th>Activity ((a_1))</th>
<th>Pure PEMA</th>
<th>PEMA + 17.5% DBP</th>
<th>PEMA + 17.5% DBS</th>
<th>PEMA + 17.5% BS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.067</td>
<td>0.011</td>
<td>0.018</td>
<td>0.020</td>
<td>0.018</td>
</tr>
<tr>
<td>0.133</td>
<td>0.026</td>
<td>0.039</td>
<td>0.043</td>
<td>0.035</td>
</tr>
<tr>
<td>0.198</td>
<td>0.044</td>
<td>0.062</td>
<td>0.067</td>
<td>0.058</td>
</tr>
<tr>
<td>0.262</td>
<td>0.067</td>
<td>0.084</td>
<td>0.093</td>
<td>0.082</td>
</tr>
<tr>
<td>0.324</td>
<td>0.087</td>
<td>0.109</td>
<td>0.121</td>
<td>0.107</td>
</tr>
<tr>
<td>0.386</td>
<td>0.109</td>
<td>0.137</td>
<td>0.151</td>
<td>0.134</td>
</tr>
<tr>
<td>0.446</td>
<td>0.132</td>
<td>0.166</td>
<td>0.184</td>
<td>0.165</td>
</tr>
<tr>
<td>0.505</td>
<td>0.158</td>
<td>0.199</td>
<td>0.221</td>
<td>0.203</td>
</tr>
<tr>
<td>0.564</td>
<td>0.188</td>
<td>0.236</td>
<td>0.264</td>
<td>0.253</td>
</tr>
<tr>
<td>0.621</td>
<td>0.219</td>
<td>0.277</td>
<td>0.308</td>
<td>0.308</td>
</tr>
</tbody>
</table>
Table 7: Activity as a function of weight fraction data for sorption of toluene in pure PEMA and plasticized PEMA

<table>
<thead>
<tr>
<th>Activity ($a_1$)</th>
<th>Weight fraction of Toluene ($w_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pure PEMA</td>
</tr>
<tr>
<td>0.061</td>
<td>0.007</td>
</tr>
<tr>
<td>0.122</td>
<td>0.020</td>
</tr>
<tr>
<td>0.182</td>
<td>0.035</td>
</tr>
<tr>
<td>0.242</td>
<td>0.046</td>
</tr>
<tr>
<td>0.302</td>
<td>0.061</td>
</tr>
<tr>
<td>0.361</td>
<td>0.074</td>
</tr>
<tr>
<td>0.420</td>
<td>0.096</td>
</tr>
<tr>
<td>0.479</td>
<td>0.119</td>
</tr>
<tr>
<td>0.537</td>
<td>0.146</td>
</tr>
<tr>
<td>0.595</td>
<td>0.176</td>
</tr>
</tbody>
</table>
Table 8: Activity as a function of weight fraction data for sorption of ethylbenzene in pure PEMA and plasticized PEMA

<table>
<thead>
<tr>
<th>Activity ($\alpha_1$)</th>
<th>Weight fraction of Ethylbenzene ($w_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pure PEMA</td>
</tr>
<tr>
<td>0.055</td>
<td>0.007</td>
</tr>
<tr>
<td>0.110</td>
<td>0.019</td>
</tr>
<tr>
<td>0.165</td>
<td>0.030</td>
</tr>
<tr>
<td>0.220</td>
<td>0.047</td>
</tr>
<tr>
<td>0.275</td>
<td>0.067</td>
</tr>
<tr>
<td>0.330</td>
<td>0.085</td>
</tr>
<tr>
<td>0.384</td>
<td>0.102</td>
</tr>
<tr>
<td>0.439</td>
<td>0.122</td>
</tr>
<tr>
<td>0.493</td>
<td>0.143</td>
</tr>
<tr>
<td>0.547</td>
<td>0.169</td>
</tr>
</tbody>
</table>
The comparison of sorption of pure polymer with respect to the addition of plasticizers in terms of activity as a function of weight fraction curves is shown in the plots below.

Figure 10: Activity as a function of weight fraction curves of benzene in PEMA and plasticized PEMA
Figure 11: Activity as a function of weight fraction curves of toluene in PEMA and plasticized PEMA.
Figure 12: Activity as a function of weight fraction curves of ethylbenzene in PEMA and plasticized PEMA
The sorption of benzene, toluene and ethylbenzene in a copolymer of poly (ethyl methacrylate) and poly (methyl methacrylate) with a 17.5% addition of plasticizers like di n-butyl phthalate, di n-butyl sebacate, n-butyl stearate are reported in table 8 to 10.

Table 9: Activity as a function of weight fraction data for sorption of benzene in pure PEMA/PMMA copolymer and plasticized copolymer

<table>
<thead>
<tr>
<th>Activity ($a_1$)</th>
<th>Weight fraction of Benzene ($w_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PEMA/PMMA</td>
<td>PEMA/PMMA + 17.5% DBP</td>
</tr>
<tr>
<td>0.067</td>
<td>0.014</td>
</tr>
<tr>
<td>0.133</td>
<td>0.029</td>
</tr>
<tr>
<td>0.198</td>
<td>0.046</td>
</tr>
<tr>
<td>0.262</td>
<td>0.061</td>
</tr>
<tr>
<td>0.324</td>
<td>0.081</td>
</tr>
<tr>
<td>0.386</td>
<td>0.100</td>
</tr>
<tr>
<td>0.446</td>
<td>0.124</td>
</tr>
<tr>
<td>0.505</td>
<td>0.147</td>
</tr>
<tr>
<td>0.564</td>
<td>0.174</td>
</tr>
<tr>
<td>0.621</td>
<td>0.209</td>
</tr>
</tbody>
</table>
Table 10: Activity as a function of weight fraction data for sorption of toluene in pure PEMA/PMMA copolymer and plasticized copolymer

<table>
<thead>
<tr>
<th>Activity ($a_1$)</th>
<th>Pure PEMA/PMMA</th>
<th>PEMA/PMMA + 17.5% DBP</th>
<th>PEMA/PMMA + 17.5% DBS</th>
<th>PEMA/PMMA + 17.5% BS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.061</td>
<td>0.007</td>
<td>0.015</td>
<td>0.017</td>
<td>0.021</td>
</tr>
<tr>
<td>0.122</td>
<td>0.020</td>
<td>0.032</td>
<td>0.036</td>
<td>0.042</td>
</tr>
<tr>
<td>0.182</td>
<td>0.034</td>
<td>0.050</td>
<td>0.056</td>
<td>0.061</td>
</tr>
<tr>
<td>0.242</td>
<td>0.050</td>
<td>0.070</td>
<td>0.077</td>
<td>0.079</td>
</tr>
<tr>
<td>0.302</td>
<td>0.066</td>
<td>0.090</td>
<td>0.100</td>
<td>0.099</td>
</tr>
<tr>
<td>0.361</td>
<td>0.082</td>
<td>0.112</td>
<td>0.124</td>
<td>0.120</td>
</tr>
<tr>
<td>0.420</td>
<td>0.099</td>
<td>0.137</td>
<td>0.151</td>
<td>0.142</td>
</tr>
<tr>
<td>0.479</td>
<td>0.118</td>
<td>0.165</td>
<td>0.180</td>
<td>0.166</td>
</tr>
<tr>
<td>0.537</td>
<td>0.142</td>
<td>0.196</td>
<td>0.214</td>
<td>0.198</td>
</tr>
<tr>
<td>0.595</td>
<td>0.169</td>
<td>0.230</td>
<td>0.250</td>
<td>0.229</td>
</tr>
<tr>
<td>Activity $(a_1)$</td>
<td>Weight fraction of Ethylbenzene $(w_1)$</td>
<td>Pure PEMA/PMMA</td>
<td>PEMA/PMMA + 17.5% DBP</td>
<td>PEMA/PMMA + 17.5% DBS</td>
</tr>
<tr>
<td>----------------</td>
<td>---------------------------------------</td>
<td>----------------</td>
<td>-----------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>0.055</td>
<td></td>
<td>0.006</td>
<td>0.013</td>
<td>0.014</td>
</tr>
<tr>
<td>0.110</td>
<td></td>
<td>0.020</td>
<td>0.030</td>
<td>0.035</td>
</tr>
<tr>
<td>0.165</td>
<td></td>
<td>0.032</td>
<td>0.045</td>
<td>0.054</td>
</tr>
<tr>
<td>0.220</td>
<td></td>
<td>0.044</td>
<td>0.062</td>
<td>0.074</td>
</tr>
<tr>
<td>0.275</td>
<td></td>
<td>0.059</td>
<td>0.081</td>
<td>0.091</td>
</tr>
<tr>
<td>0.330</td>
<td></td>
<td>0.075</td>
<td>0.105</td>
<td>0.110</td>
</tr>
<tr>
<td>0.384</td>
<td></td>
<td>0.091</td>
<td>0.129</td>
<td>0.131</td>
</tr>
<tr>
<td>0.439</td>
<td></td>
<td>0.108</td>
<td>0.154</td>
<td>0.161</td>
</tr>
<tr>
<td>0.493</td>
<td></td>
<td>0.128</td>
<td>0.180</td>
<td>0.189</td>
</tr>
<tr>
<td>0.547</td>
<td></td>
<td>0.158</td>
<td>0.200</td>
<td>0.219</td>
</tr>
</tbody>
</table>
The comparison of sorption of pure copolymer with respect to the addition of plasticizers in terms of activity vs weight fraction curves is shown in the plots below.

**Figure 13: Activity as a function of weight fraction curves of benzene in PEMA/PMMA copolymer and plasticized copolymer**
Figure 14: Activity as a function of weight fraction curves of toluene in PEMA/PMMA copolymer and plasticized copolymer
Figure 15: Activity as a function of weight fraction curves of ethylbenzene in PEMA/PMMA copolymer and plasticized copolymer
The Flory-Huggins model is fit to the experimental data. Interaction parameters are reported in tables 11 and 12.

**Table 12: Interaction parameters after Flory-Huggins modelling along with the adjustable parameter used in each solvent for PEMA**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pure PEMA</th>
<th>PEMA+17.5% DBP</th>
<th>PEMA+17.5% DBS</th>
<th>PEMA+17.5% BS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi_{12})</td>
<td></td>
<td></td>
<td></td>
<td>0.066</td>
</tr>
<tr>
<td>(\chi_{13})</td>
<td></td>
<td>0.170</td>
<td>0.077</td>
<td>0.163</td>
</tr>
<tr>
<td></td>
<td>Benzene</td>
<td></td>
<td>0.396</td>
<td>0.174</td>
</tr>
<tr>
<td>(\chi_{23})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha)</td>
<td></td>
<td></td>
<td></td>
<td>0.236</td>
</tr>
<tr>
<td>(\chi_{12})</td>
<td></td>
<td></td>
<td></td>
<td>0.128</td>
</tr>
<tr>
<td>(\chi_{13})</td>
<td>Toluene</td>
<td></td>
<td>0.267</td>
<td>0.098</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.742</td>
<td>0.326</td>
</tr>
<tr>
<td>(\chi_{23})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha)</td>
<td></td>
<td></td>
<td></td>
<td>0.443</td>
</tr>
<tr>
<td>(\chi_{12})</td>
<td></td>
<td></td>
<td></td>
<td>0.112</td>
</tr>
<tr>
<td>(\chi_{13})</td>
<td>Ethylbenzene</td>
<td></td>
<td>0.240</td>
<td>0.092</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.454</td>
<td>0.199</td>
</tr>
<tr>
<td>(\chi_{23})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha)</td>
<td></td>
<td></td>
<td></td>
<td>0.271</td>
</tr>
</tbody>
</table>
Table 13: Interaction parameters after Flory-Huggins modelling along with the adjustable parameter used in each solvent for PEMA/PMMA copolymer

<table>
<thead>
<tr>
<th></th>
<th>Pure PEMA/PMMA</th>
<th>PEMA/PMMA + 17.5% DBP</th>
<th>PEMA/PMMA + 17.5% DBS</th>
<th>PEMA/PMMA + 17.5% BS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_{12}$</td>
<td>0.110</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\chi_{13}$</td>
<td>0.192</td>
<td>0.087</td>
<td>0.185</td>
<td></td>
</tr>
<tr>
<td>$\chi_{23}$</td>
<td></td>
<td>0.212</td>
<td>0.057</td>
<td>0.340</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.268</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\chi_{12}$</td>
<td></td>
<td></td>
<td></td>
<td>0.141</td>
</tr>
<tr>
<td>$\chi_{13}$</td>
<td></td>
<td>0.248</td>
<td>0.091</td>
<td>0.249</td>
</tr>
<tr>
<td>$\chi_{23}$</td>
<td></td>
<td>0.325</td>
<td>0.088</td>
<td>0.523</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.411</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\chi_{12}$</td>
<td></td>
<td></td>
<td></td>
<td>0.183</td>
</tr>
<tr>
<td>$\chi_{13}$</td>
<td></td>
<td>0.315</td>
<td>0.121</td>
<td>0.255</td>
</tr>
<tr>
<td>$\chi_{23}$</td>
<td></td>
<td>0.281</td>
<td>0.076</td>
<td>0.451</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.355</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where, $\alpha$ - correction factor varying from 0 to 1, which is obtained by minimizing difference between experimental and model activity

$\chi_{12}$ - solvent-polymer interaction parameter

$\chi_{13}$ - solvent-plasticizer interaction parameter

$\chi_{23}$ - polymer-plasticizer interaction parameter

With the sorption data and Flory-Huggins thermodynamic correlations, the partition coefficient at infinite dilution in the gas phase was calculated as:\(^{19}\):

$$K^\infty = \left[ \frac{\rho_2 RT}{\Omega_1^\infty M_1 P_{1 sat}} \right]$$

(33)

$K^\infty$ is the partition coefficient at infinite dilution. $P_{1 sat}$ is the saturated vapor pressure of the solvent, $M_1$ is the molecular mass of the solvent, $\Omega_1^\infty$ is the weight based infinite dilution activity coefficient.

$$\Omega_1^\infty = \gamma_1^\infty \frac{M_2 x_2 + M_3 x_3}{M_1}$$

(34)

$$\alpha_1 = \gamma_1 x_1$$

(35)

From equation 25 and equation 28, $\gamma_1^\infty$ is calculated by calculating the limit of $\gamma$ with $x_1$ going to 0 for binary and ternary system respectively.

$$\ln \gamma_1^\infty = \ln \frac{V_1}{V_2 x_2 + V_3 x_3} + 1 - \frac{V_1}{V_2} \phi_3 - \frac{V_1}{V_2} \phi_2 + (\chi_{13} \phi_3 + \chi_{12} \phi_2) - \chi_{23} \frac{V_1}{V_3} \phi_2 \phi_3$$

(36)

With the help of above equations, $K^\infty$ is calculated for all the polymer/plasticizer blends that are considered and are listed in the tables below.

**Table 14: Partition coefficients at infinite dilution of PEMA and plasticized PEMA**

<table>
<thead>
<tr>
<th></th>
<th>PEMA</th>
<th>PEMA + DBP</th>
<th>PEMA + DBS</th>
<th>PEMA + BS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benzene</strong></td>
<td>1182.60</td>
<td>1278.71</td>
<td>1293.40</td>
<td>1302.28</td>
</tr>
<tr>
<td><strong>Toluene</strong></td>
<td>935.77</td>
<td>1036.19</td>
<td>1051.74</td>
<td>1055.55</td>
</tr>
<tr>
<td><strong>Ethylbenzene</strong></td>
<td>814.82</td>
<td>903.59</td>
<td>919.42</td>
<td>928.40</td>
</tr>
</tbody>
</table>
Table 15: Partition coefficients at infinite dilution of copolymer and plasticized copolymer

<table>
<thead>
<tr>
<th></th>
<th>PEMA/PMMA</th>
<th>PEMA/PMMA+ 17.5% DBP</th>
<th>PEMA/PMMA+ 17.5% DBS</th>
<th>PEMA/PMMA+ 17.5% BS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1131.60</td>
<td>1221.98</td>
<td>1245.72</td>
<td>1249.64</td>
</tr>
<tr>
<td>Toluene</td>
<td>923.22</td>
<td>1007.67</td>
<td>1034.54</td>
<td>1032.86</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>770.75</td>
<td>848.02</td>
<td>873.89</td>
<td>871.43</td>
</tr>
</tbody>
</table>

The partition coefficients at infinite dilutions, clearly show more sorption with the addition of a plasticizer. It is also evident that DBS and BS show more sorption than DBP. Literature\textsuperscript{20} states that the structure of plasticizer effects the extent of sorption. Straight-chained plasticizers show more sorption when compared to branched or ring structures, due to less viscosity between the molecules. Also, the plasticizers with higher molecular mass tend to show higher sorption of organic vapors. From tables 2 and 3, it can be understood that DBS and BS having liner structure and higher molecular mass, show a comparatively higher sorption than DBP. The molecular weights and the structures being similar for DBS and BS, they show similar trends in sorption of organic vapors.
CHAPTER 5: CONCLUSION AND FUTURE WORK

5.1 Conclusion

This thesis work reported the sorption data of poly (ethyl methacrylate) and a copolymer of poly (ethyl methacrylate) and poly (methyl methacrylate), with three different plasticizers at 17.5% composition at 298.15K. The molecular mass and the structure of the plasticizers effected the sorption of VOCs into the polymer film. The results are interpreted by fitting the Flory Huggins model to the experimental data.

5.2 Future Work

Similar work can be continued on other glassy polymers with different plasticizer combinations and compositions. Observing viscoelastic properties on these plasticized polymers and calculate the viscoelastic modulus, helps in analyzing the polymer/plasticizer combinations for more sorption with fewer attenuation losses. Efficient LabVIEW code can be written for the automation of sorption to measure the viscoelastic properties using an impedance analyzer. Detection of hydrocarbons in liquid phase is another possible area to work on.
REFERENCES

(1) Thompson, M.; Stone, D. *Surface-Launched Acoustic Wave Sensors*; A Wiley Interscience publication.


(11) Adhikari, P.; Alderson, L.; Bender, F.; Ricco, A. J.; Josse, F. Investigation of Polymer-Plasticizer Blends as SH-SAW Sensor Coatings for Detection of Benzene in Water with High Sensitivity and
https://doi.org/10.1021/acssensors.6b00659.


(13) Wong, H. C.; Campbell, S. W.; Bhethanabotla, V. R. Sorption of Benzene, Dichloromethane, n-Propyl Acetate, and 2-Butanone by Poly (Methyl Methacrylate), Poly (Ethyl Methacrylate), and Their Copolymers at 323.15 K Using a Quartz Crystal Balance. **2011**, 4772–4777.


https://doi.org/10.1039/a703601i.
APPENDIX A: ADDITIONAL INFORMATION

All the plots that explain the model fit to the experimental data are provided in this section.

1. Pure poly (ethyl methacrylate) (PEMA) binary data:

![Pure PEMA - Benzene graph]

**Figure a1:** Comparison of model vs experimental data of benzene in pure PEMA
Figure a2: Comparison of model vs experimental data of toluene in pure PEMA
Figure a3: Comparison of model vs experimental data of ethylbenzene in pure PEMA
2. Pure copolymer of poly (ethyl methacrylate) and poly (methyl methacrylate) (PEMA/PMMA) 

binary data:

Figure a4: Comparison of model vs experimental data of benzene in pure PEMA/PMMA copolymer
Figure a5: Comparison of model vs experimental data of toluene in pure PEMA/PMMA copolymer
Figure a6: Comparison of model vs experimental data of ethylbenzene in pure PEMA/PMMA copolymer
3. Poly (ethyl methacrylate) (PEMA) with 17.5% of di n-butyl phthalate (DBP):

![Comparison of model vs experimental data of benzene in PEMA with 17.5% DBP](image)

**Figure a7: Comparison of model vs experimental data of benzene in PEMA with 17.5% DBP**
Figure a8: Comparison of model vs experimental data of toluene in PEMA with 17.5% DBP
Figure a9: Comparison of model vs experimental data of ethylbenzene in PEMA with 17.5% DBP
4. Poly (ethyl methacrylate) (PEMA) with 17.5% of di n-butyl sebacate (DBS):

![Graph](image)

*Figure a10: Comparison of model vs experimental data of benzene in PEMA with 17.5% DBS*
Figure a11: Comparison of model vs experimental data of toluene in PEMA with 17.5% DBS
Figure a12: Comparison of model vs experimental data of ethylbenzene in PEMA with 17.5% DBS
5. Poly (ethyl methacrylate) (PEMA) with 17.5% of n-butyl stearate (BS):

Figure a13: Comparison of model vs experimental data of benzene in PEMA with 17.5% BS
Figure a14: Comparison of model vs experimental data of toluene in PEMA with 17.5% BS
Figure a15: Comparison of model vs experimental data of ethylbenzene in PEMA with 17.5% BS
6. Copolymer of poly (ethyl methacrylate) and poly (methyl methacrylate) (PEMA/PMMA) with 17.5% of di n-butyl phthalate (DBP):

Figure a16: Comparison of model vs experimental data of benzene in PEMA/PMMA copolymer with 17.5% DBP
Figure a17: Comparison of model vs experimental data of toluene in PEMA/PMMA copolymer with 17.5% DBP
Figure a18: Comparison of model vs experimental data of ethylbenzene in PEMA/PMMA copolymer with 17.5% DBP
7. Copolymer of poly (ethyl methacrylate) and poly (methyl methacrylate) (PEMA/PMMA) with 17.5% of di n-butyl sebacate (DBS):

Figure a19: Comparison of model vs experimental data of benzene in PEMA/PMMA copolymer with 17.5% DBS
Figure a20: Comparison of model vs experimental data of toluene in PEMA/PMMA copolymer with 17.5% DBS
**Figure a21:** Comparison of model vs experimental data of ethylbenzene in PEMA/PMMA copolymer with 17.5% DBS
8. Copolymer of poly (ethyl methacrylate) and poly (methyl methacrylate) (PEMA/PMMA) with 17.5% of n-butyl stearate (BS):

Figure a22: Comparison of model vs experimental data of benzene in PEMA/PMMA copolymer with 17.5% BS
Figure a23: Comparison of model vs experimental data of toluene in PEMA/PMMA copolymer with 17.5% BS
Figure a24: Comparison of model vs experimental data of ethylbenzene in PEMA/PMMA copolymer with 17.5% BS