DEVELOPMENT OF A PIEZOELECTRIC QUARTZ CRYSTAL MICROBALANCE FOR THE MEASUREMENT OF PENETRANT SORPTION INTO POLYMERS

By

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CHAPTER I

INTRODUCTION

A basic understanding of molecular diffusion in polymer-solvent systems is important in the design and analysis of many industrial polymer processes. The very high viscosities that are characteristic of polymer systems make enhancement of mass transfer by mechanical means difficult; thus, mass transfer by diffusion is the rate controlling factor in many processes. An example is polymer production reactors where the rate of the free radical chain addition reaction may be determined by the diffusion of the reactant through the highly viscous polymer-monomer mixture. Limited conversion and premature termination of polymerization due to vitrification are reflections of sharp decreases in the diffusivity as the molecular weight in the reaction mixture increases.

Another example is the devolatalization process, where small amounts of residual species such as monomers or other low molecular weight chemicals present during polymerization are removed from the polymer product. The molecular diffusion of the volatile component is normally the rate limiting step of the process.

The drying of coatings is also limited by the ability of a solvent to diffuse to the surface, and often the physical properties of coatings are influenced significantly by the presence of even trace amounts of solvents.

Materials such as polyimides are used in the microelectronics industry since such applications require planarity, insulating ability and thermal stability. Sorption of ambient water vapor can substantially change the dielectric constant of a polyimide. The maximum water uptake provides an upper limit on the dielectric constant of the material and therefore affects the performance of the polymer film as an insulator (Moylan et al., 1991). Diffusion data are also useful in studying the barrier properties of polymers in packaging applications since the packaging material must not only prevent loss of essential flavors and fragrances from the product itself, but must also protect the product from external sources of contamination (Gillette, 1988).

Other technological applications of polymers that require diffusion data are polymer modified electrodes doped with electrically conducting polymers. Photolithography relies on differences in the diffusion behavior of small molecules in the exposed region relative to the virgin film material. Finally, improved understanding of diffusion could have an impact on the molecular biology of cell recognition and drug delivery. Therefore diffusion of penetrants into polymers is of extreme practical interest.

The piezoelectric quartz crystal microbalance technique discussed in this work is a new method for the measurement of sorption of penetrants into polymers. Diffusion of solvents into polymers can be studied by measuring the sorption of the solvent into the polymer as a function of time. Over the years, sorption of solvents in polymers has been measured by various techniques. However these techniques have limitations. A review of the techniques and their limitations is presented in the next chapter. In the piezoelectric quartz crystal method, an oscillating quartz crystal is used as a microbalance. A very thin film of the polymer is coated on the crystal and exposed to a penetrant vapor atmosphere. An advantage of this technique is that quartz crystals are very sensitive to any change in the mass on the crystal. Weight changes that occur due to diffusion of the penetrant into the polymer film are measured by recording the change in frequency of the vibrating crystal.

The objectives of this work were to design and build an apparatus that could be used for measuring the rate of sorption of penetrants into polymers using a piezoelectric quartz crystal microbalance. One of the important features of this apparatus is that all the parts used are commercially available. The ultimate aim of this and subsequent research is to provide engineers with an accurate, easy to use method for measuring the diffusivity of penetrants into polymers.

The next chapter in this thesis is the Literature Review, where the various methods used for measurement of sorption, some of the polymer-solvent systems previously studied, and experimental apparatus using the piezoelectric quartz crystal are reviewed. Chapter III explains the basis of using the piezoelectric quartz crystal as a microbalance for measuring small changes in mass. Chapter IV describes the experimental apparatus in detail. Chapter V presents and discusses the results obtained using this apparatus. Chapter VI presents the conclusions drawn from the results. In chapter VII, are given, recommendations to improve the apparatus to obtain better results. The data obtained for the various systems studied, the procedure for running the experiment, and a detailed list of the components used to build the apparatus are given in the Appendices.

CHAPTER II

LITERATURE REVIEW

Sorption of penetrants into polymers has been a subject of study for the past several decades. During this period, various methods have been used to study the sorption characteristics of various polymer-solvent systems. The intent of this literature review was to study the methods that have been used for the study of sorption of penetrants into polymers and the various polymer-solvent systems previously studied. This literature review also explains the necessity for building a new apparatus for the study of sorption of solvents into polymers. The various methods are described and their limitations are listed. These limitations are the driving force for building a new apparatus for the study of sorption of penetrants into polymers.

The process of sorption can be described by the constitutive laws of diffusion. The diffusion coefficient is the basic physical quantity that describes the process of sorption. The diffusion coefficient can be obtained by measuring the weight sorbed, M(t) by the polymer film as a function of time t. A characteristic curve of weight sorbed versus square root of time can be plotted for a polymer-solvent system. This curve is known as the "reduced sorption curve". The shape of this curve can be used to characterize the type of sorption that is taking place for a particular polymer-solvent system. When the shape of the curve satisfies the following conditions the sorption that is taking place is said to be 'Fickian' or 'normal' (Park, 1968):

- The sorption curve should be linear in the initial portion of the curve. In the case of absorption it should be linear for about 60 % of the curve.
- Above the linear portion of the curve, the second derivative of the curve should always be negative.
- The sorption curves should be superimposable for films of different thicknesses.

When the curve does not conform to these conditions the sorption is said to be "anomalous". The shape of the curve for anomalous diffusion has been observed to be either sigmoid, two stage, or pseudo-Fickian. In the case of sigmoid shaped curves, the sorption curve is 'S' shaped. Pseudo-Fickian curves resemble Fickian curves but the initial linear part of the curve is limited. Also the equilibrium amount of solvent sorbed is approached slowly.

In the case of two stage sorption curve, an initial portion occurs where sorption takes place rapidly and seems to reach equilibrium. After which sorption proceeds slowly to the point of true equilibrium. When the behavior of the polymer-solvent system is extremely non-Fickian, it is said to be case-II transport. A schematic diagram of the various sorption curves observed is given in Figure 1.

Some of the methods that have been used for the study of sorption of penetrants into polymers along with their limitations are reviewed below.

Permeation

In this method a polymer film is inserted in between two evacuated

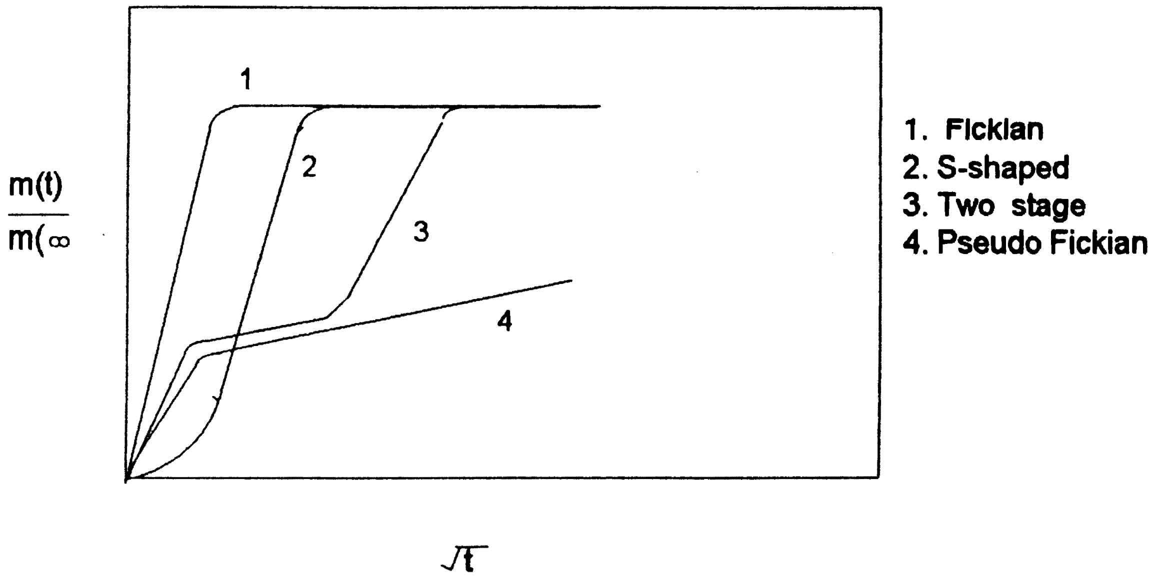

Figure 1. Qualitative Representation of Reduced Sorption Curves

chambers. Vapor is suddenly introduced into one of the chambers at a specified pressure. The amount of vapor that permeates the film is then measured as a function of time. The steady permeation rate and time lag are used to calculate the diffusivity (Park, 1968).

The permeation technique cannot be used when the experiments have to be carried out for a long time as problems can arise due to leakage and membrane distortion. Problems can also arise when the membrane is not sealed properly or if the supporting grids of the membrane do not allow uniform pressure to be exerted on the membrane. Complications can also occur if there are small holes in the membrane as these can alter the rate of permeation.

Refractive Index Techniques

This technique is used more often to describe the concentration-distance relationship in the case of non-steady state diffusion (Crank and Park, 1968). Concentration-distance curves are particularly suitable where the whole concentration range from pure solvent to pure polymer is being investigated. The refractive index provides a measure of concentration in systems where the relationship between the refractive index and the concentration is known. Usually, a thin polymer sheet is clamped between glass plates and the mounted film is immersed in solution or penetrant. The sharp localized fringes which are produced with a suitable optical assembly can be examined and photographed with a standard microscope. Each film is a contour line of the refractive index and the interference pattern can be used to construct refractive index distance curves. Concentration-distance relationships are obtained from these data which are used to calculate diffusion coefficients.

The disadvantage with this method is that a doubling of the interference fringes is obtained. Also the microscope that is used to see the fringes has to be focused differently for high and low refractive index gradients. This makes this method quite complicated.

Laser Interferometry

Laser interferometry is a technique which can be used to find the type of diffusion that is occurring in a polymer-solvent system using a laser at a fixed polarization and angle of incidence (Saenger and Tong, 1991). The principle involved is that a change in the product of the film thickness and refractive index can be quantitatively determined from the change in the optical path length difference between interfering reflections from the front and back surfaces of the film. Diffusion related properties such as solvent uptake-swelling, dissolution, and drying rates are accessible through this method.

The disadvantage of this method is that the analysis of the data to obtain diffusion coefficients is complicated and has not been described in detail in the literature.

Radiation Absorption Methods

The concentration of a colored diffusant at any point can be measured by the intensity of the light that is transmitted at that point. A photometer system can be used to obtain the concentration-distance curves. Radiation absorption methods can be applied either to the study of the diffusion of colored organic solvents or in the study of diffusion of dyes.

This method was used in the study of the concentration-distance relationships of methyl iodide in cellulose acetate and poly(vinyl acetate) sheets during vapor sorption experiments (Long and Richman, 1960). The polymer film was quenched in liquid nitrogen at the required stage in sorption. Parallel sided sections were cut and the sections were mounted in intimate contact with a photographic plate and exposed to a collimated beam of X-rays. Methyl iodide absorbs the X-rays and blackening is produced on the surface of the plate. This blackening is inversely proportional to the iodide content. A microdensitometer was used to construct the concentration-distance curves for the system. Interpretation of the data in this technique is quite difficult in terms of diffusion coefficient since a relationship between concentration and diffusion coefficient has to be assumed.

Radiometry has also been used to study diffusion in polymers (Joks, 1987). In radiometry, the specimens are placed in a solution labeled with a radioisotope for a given time and at a fixed temperature. The specimens are then taken out of the solution, dried, and placed in measuring vials. The sorbed substance which is labeled with the radioisotope is extracted and its radioactivity measured. The radioactivity is proportional to the mass of the substances diffusing into the polymer.

Radiotracer Methods

Useful information about the mobility of molecules can be obtained from the study of diffusion in the absence of any overall gradient of chemical composition. These type of measurements are made by using a gradient concentration of a labeled compound when the total amount of that compound is constant throughout the system.

In this method a very thin film of C^{14} labeled polymer is applied from a benzene solution on top of a thick film of unlabeled polymer. At the beginning of the experiment when no diffusion has occurred about half the β particles escape from the surface, but as the labeled molecules diffuse deeper into the composite film more of the emitted β particles are absorbed. The resulting activity-time relationship is measured with a thin end window Geiger tube.

> "Assuming that the β particle absorption follows a logarithmic law, theoretical curves of log (Dt) against log (I) can be constructed, where I is the observed activity. On comparing these curves with the experimental values of log t versus log I, values of D can be obtained."(Park and Crank, 1968)

One of the disadvantages of this method is that we have to work with radioactive materials. This technique can be used only when materials can be labeled.

Forced Raleigh Scattering

One of the recently developed optical methods, forced Raleigh scattering (FRS) can be used to measure tracer diffusion coefficients in polymer-solvent mixtures.

> "This transient optical grating technique creates a spatially periodic concentration profile of photochromic dyes, and subsequently follows its dispersion by diffusion. It is a three step procession. In the first step, two intense, mutually coherent laser beams of wavelength λ intersect at an angle θ in the sample, producing an interference pattern sinusoidal in intensity with a period. In the second step, the pattern is recorded in the sample by the presence

> of a small quantity of photochromic dye moieties, as those dye molecules, A, in the constructive interference fringes undergo isomerization to a spectrally distinct form B. The resulting sinusoidal concentration profile of A and B acts as an optical grating. In the third step, a third laser beam is directed through the grating and the diffracted intensity is monitored. The diffracted intensity decays exponentially in time as the grating is erased by the interdiffusion of the two dye isomers A and B. The decay time constant depends directly on the dye diffusion coefficient. This decay follows a functional form which relates the measured photo voltage V(t) and the time constant t. A plot of t v/s d^2 gives us the value of D." (Huang et al., 1987)

The FRS technique can be used only to probe single molecule behavior and cannot be used in more general applications of industrial importance.

Gravimetric Sorption

The sorption experiment is one of the most widely used methods of measuring the solubility and diffusivity in a polymer-solvent system. It is usually obtained by weighing the uptake of vapor by the polymer. For a simple polymer specimen geometry and constant vapor pressure, the rate of approach to equilibrium gives a direct measure of the diffusion coefficient (Crank and Park, 1968).

The simplest method for these type of experiments would be to weigh the polymer as the solvent is absorbed. For this purpose, a specimen of known shape and size is kept in a constant pressure atmosphere of penetrant. The sample can be withdrawn and weighed from time to time, but serious error is introduced due to the presence of air. The weight measurements will not be very accurate because the sample is removed from the penetrant atmosphere from time to time. These errors can be overcome by conducting the experiment under more precisely controlled conditions.

A refined sorption apparatus was used by Duda et al. (1973) for measuring the diffusion coefficients for molten polymers. The sorption chamber consisted of a cylindrical column with two quartz springs with polymer samples contained in the inner chamber. The polymer samples were contained in cylindrical quartz buckets which were suspended by the springs. The two annular spaces which surround the inner chamber of the sorption column were used to control the temperature inside the sample chamber via a condensing fluid. Specially designed manometers and pressure controllers were used to control the pressure inside the system. The penetrant feed system consisted of an insulated flask with a temperature control system which controlled the liquid penetrant temperature. The valve and tubing between the feed system and the sorption chamber were heated to prevent condensation of vapor. The weight change of the samples was followed as a function of time by measurement of the spring extension with a cathetometer.

One of the disadvantages of this method is that only the chamber in which the polymer film is kept can be heated. The polymer film is heated by convection and conduction of the penetrant vapor and the temperature of the film may differ significantly from the temperature of the chamber as sorption proceeds. Also this apparatus cannot be interfaced with a computer to collect data at very small intervals of time.

Another experimental apparatus that made use of the gravimetric sorption technique was the one used by Doong and Ho (1991). The apparatus used was a Cahn 2000 electrobalance to monitor the weight change. The electronic components of the flow balance chamber were purged with an inert N_2 gas stream. For the penetrant stream, a N_2 stream was bubbled through a liquid penetrant saturator and was mixed with a second stream of nitrogen gas to give the desired partial pressure of the penetrant. A constant temperature oven was used to heat the liquid saturator. The polymer sample was placed in a pan with a hangdown wire connected to the balance and enclosed in a split tube furnace. All the incoming lines were wrapped in heating tape to prevent condensation of the vapor. The measured weight change, temperature, and pressure were acquired using a data acquisition unit. In this method the penetrant must be introduced with a liquid N_2 stream otherwise it will damage the microbalance. If the hangdown wire touches the split tube furnace, readings will not be very accurate. Also this method requires a considerable amount of time to reach equilibrium due to the large sample required and low diffusivity of the penetrant.

A sorption technique that involved the piezoelectric quartz crystal microbalance was developed by Moylan et al. (1991) to measure the solubility and diffusion coefficients of water in polyimides. Their apparatus used a quartz crystal microbalance to measure the small mass changes by incorporating the sensor into a vacuum system mounted inside a constant temperature bath. The quartz crystal was coated with a known thickness of polymer film. This thickness was measured using a profilometer. Their apparatus consisted of an Inficon Compact QCM sensor and feedthrough which was attached to a home-built adapter with two electrical feedthroughs. The electrical feedthrough was attached to a thin film heater that was used to heat the sample. The sensor assembly was mounted onto a vacuum system that includes a foreline, the main chamber, a leak valve between the two, and an exhaust manifold with a small oil diffusion pump. Pressures in the foreline and chamber were measured using pressure transducers. The sample inlet section had a direct bypass line to the manifold so that samples could be degassed while the chamber and foreline were still under vacuum. For the determination of mass uptake by a thin film, the mass per unit area is divided by the film thickness to yield a mass uptake per unit volume. The disadvantage of this apparatus is that some of the components are not commercially available hence duplicating the apparatus will be difficult.

The merits of the quartz crystal microbalance relative to the quartz spring balance, the most common means of measuring diffusivity in polymers, are given in Table I.

TABLE I

RELATIVE MERITS OF THE QUARTZ CRYSTAL MICROBALANCE OVER THE QUARTZ SPRING BALANCE

Quartz Crystal Microbalance	Quartz Spring Balance
Can measure weight changes as low as 10^{-12} grams	Cannot measure such low changes in weight
Can be easily interfaced to a computer	Very difficult to interface it to a computer
Thinner films can be used for experimentation(10 microns thick)	Films have to be 50-100 microns thick
Time required for one experiment 12-15 hours	Time required to conduct an experiment 3-5 days

Diffusion Studies in Various Polymer-Solvent Systems

The first systematic study of sorption of organic vapors in polymers was made by Prager and Long (1951). They studied the sorption of six hydrocarbons (propane, n-butane, isobutane, n-pentane, isopentane and neopentane) in polyisobutylene at 35°C, which is approximately 110°C above the glass transition temperature of this polymer. The sorption curves determined in the experiment were of Fickian nature which could be expected given the experimental temperature. Reproducibility was good in the case of propane, n-pentane, isooctane and neopentane and not very good for n-pentane and isopentane. The diffusion coefficients were found to increase rapidly with concentration. It was assumed that the polymer film does not swell during sorption and the effect due to convection has been neglected. Prager and Long stated that the assumptions are justified since the penetrant concentrations used were very low.

Mandelkern and Long (1951) studied the rate of sorption of organic vapors by films of cellulose acetate. They dealt in detail with the sorption of vapors of methylene chloride and acetone by films of cellulose acetate as a function of vapor pressure, film thickness, and temperature. They observed that films that are not completely dry exhibit a much faster sorption rate. They also observed that the rate of uptake changes largely with change in pressure.

Sorption-desorption experiments were carried out by Kokes and Long (1953) at 40^{o}C with poly(vinyl acetate) and the following organic vapors: 1-propanol, propyl chloride, propylamine, isopropylamine, allyl chloride, benzene and carbon tetrachloride. All systems showed Fickian diffusion and the diffusion coefficient was found to increase with concentration. In the case of allyl chloride the sorption plot showed a slight curvature at the beginning of the experiment although the corresponding desorption plot was linear.

Drechsel et al. (1953) studied the diffusion of acetone into cellulose nitrate. They concluded that the diffusion of acetone into cellulose acetate was decidedly non-Fickian. The rate of diffusion varied with the film thickness, and it also increased strongly as the acetone vapor pressure increased. Successive sorption desorption cycles showed a decrease in the rate of sorption.

Park (1953) studied the diffusion behavior of volatile solvents into polystyrene and cellulose acetate by following the increase in mass of a polymer sheet suspended from a quartz spring in an atmosphere of vapor. A tenfold change in the molecular weight of polystyrene did not alter the sorption rate. A considerable increase in the rates of both sorption and desorption was obtained by increasing the pressure of the solvent vapor.

Cutler and McLaren (1953) studied the permeation through and sorption of organic vapors by polymers. They measured the sorption of ethanol, methanol, water, propionitrile into poly(vinyl alcohol), polystyrene, poly(vinyl chloride) and polyethylene. They presented the diffusion coefficients for the systems - styrene-water, nylon-water, nylon-ethanol, poly(vinyl chloride)-water.

Bagley and Long (1954) studied the sorption and desorption of organic vapors into cellulose acetate. They observed that the rate of sorption and desorption of acetone and methanol vapors into films of cellulose acetate exhibit a two stage behavior. When the initial concentration of the penetrant in the film was above a minimum value, the rate of sorption was large and then decreased abruptly as sorption proceeded. During the fast, initial, Fickian stage of sorption the vapor penetrated the entire polymer film to a quasi-equilibrium state. The diffusion coefficients calculated from the first stage were independent of thickness of the film. The second stage of sorption and desorption did not obey Fick's law. For constant concentration intervals, the initial rate of the second stage was found to be independent of the initial concentration of the penetrant.

Richmann and Long (1959) used a microradiographic technique to determine the concentration gradients of vapors in polymers. They applied the procedure to study the diffusion of methyl iodide into poly(vinyl acetate) at temperatures above the glass transition temperature. The diffusion was observed to be Fickian. One important result of this experiment was that it showed that the assumption of an equilibrium concentration of the penetrant at the polymer surface during sorption was valid. Studies were made for the sorption of methyl iodide into films of poly(vinyl acetate) at 20^{o}C and films of cellulose acetate at 40^{o}C. Both systems exhibited characteristic anomalous behavior which normally accompanies diffusion of organic vapors into glassy polymers.

Kishimoto and Matsumoto (Crank and Park, 1968) studied the system poly(vinyl acetate)-allyl chloride at 40°C and 5 different vapor pressures ranging from 43.3 to 196 mm Hg with films of different thicknesses. The curves for different thicknesses did not superimpose and their initial slopes for the reduced sorption curve shows an increase with increasing thickness. However, the curve had an appearance consistent with Fickian diffusion. For 43.3 mm Hg the system showed non-Fickian characteristics.

Duda and Vrentas (1968) studied the diffusion in atactic polystyrene above the glass transition temperature. Diffusivities were measured in the system n-pentane-polystyrene for low penetrant concentrations at several temperatures. Data at 760 mm Hg were collected over a temperature range of 140°C to 170°C. The diffusion coefficients were in the range of $2.59\text{x}10^{-8}$ to $1.70\text{x}10^{-7}\text{cm}^2/\text{sec}$.

Anomalous transport of hydrocarbons in polystyrene was studied by Holley et al. (1970). The transport kinetics and equilibrium concentrations of n-pentane at high penetrant activities in cast and annealed polystyrene were determined and compared with similar measurements in biaxially oriented polystyrene. The sorption of normal hydrocarbons by both biaxially oriented and cast annealed polystyrene was found to be a case II transport process. The sorption rate of normal alkanes in biaxially oriented polystyrene was three to four times more rapid than the rate in cast annealed polymers. In both types of polystyrene, the sorption mechanism changed from case II to Fickian transport process as the penetrant activity was reduced. Increasing penetrant molecular weight and branching of the penetrant decreases the sorption rate in both the types of polystyrenes.

Duda and Vrentas (1970) presented a detailed report on the various studies made on polystyrene. They presented the various polystyrene-solvent systems studied along with possible explanations for their behavior. They stated that depending on the activity of the penetrant and the temperature at which the studies were carried out, the polymer-solvent systems show Fickian and non-Fickian diffusion. They state that at low penetrant activities and at temperatures below the glass transition temperature small inert penetrants like water show Fickian behavior. They state that polystyrene-hydrocarbon systems show anomalous behavior below the glass transition temperature. They cited the work done by Alfrey and coworkers on polystyrene-acetone system where it is said that the system shows case II transport behavior.

Kwei and Wang (1972) studied the diffusion of toluene in compression molded, quench rolled, and cold drawn polyethylene films using the successive vapor absorption method. On plotting the equilibrium absorption values at various vapor pressures, they found that for the quench rolled and cold drawn films, the plots were linear within experimental error whereas that for compression molded film appeared to show a little curvature. The diffusion coefficient was found to increase exponentially with vapor concentration in compression molded film. It was independent of concentration for the cold drawn material, but increased linearly with concentration for the quench rolled films.

Duda and Ni (1977) studied the diffusion of ethylbenzene in molten polystyrene. Mutual diffusion coefficients were measured for a temperature range of 115.5-178°C. The experiments were carried out using a quartz spring sorption apparatus which had been modified for high temperature measurements. The data illustrated a strong concentration dependence of the diffusivity. This concentration dependence was more pronounced at lower temperatures and lower solvent concentrations. Duda and Ni (1979) also studied the diffusion of toluene in molten polystyrene. Diffusivity data for the system in the temperature range of 110-178°C and for concentrations as high as 80 wt% were presented. A strong concentration dependence of the diffusivity at low solvent mass fractions was indicated. The change in the mutual diffusion coefficient with mass of toluene was more pronounced at lower temperatures and lower solvent concentrations.

Aboul-Nasr and Huang (1979) studied the diffusivity and solubility of organic vapors in modified polyethylene films. They measured the steady state weight increase in a polymer film exposed to penetrant vapors using an electrobalance. They have given a detailed explanation of the technique and the method of analysis of the results and diffusivity data obtained. They found the diffusion coefficients for benzene, hexane, and heptane in modified polymers at infinite dilution. They found that the diffusivity values were highest for benzene and lowest for heptane for all films, and benzene was most affected by changes in temperature

Ju et al.(1981) used the step change sorption experiment to find diffusivities of various solvents in poly(vinyl acetate), poly(methyl methacrylate) and polystyrene. The poly(methyl methacrylate) and polystyrene data were obtained using a high temperature quartz spring sorption apparatus and the poly(vinyl acetate) data were collected using an automated Cahn electrobalance system. The systems that were studied were poly(vinyl acetate)-tetrahydrofuran, poly(methyl methacrylate)-ethanol, poly(vinyl acetate)-chloroform, poly(vinyl acetate)-toluene, poly(methyl methacrylate-toluene, polystyrene-carbondisulphide. Vrentas et al.(1984) also studied the diffusion of solvents in polyethylene. Diffusivity data were collected in the temperature range of 125-175°C. The diffusion coefficient was found to increase slightly as the solvent concentration increased at all temperatures.

Vrentas et al. (1984) studied the anomalous sorption in poly(ethyl methacrylate). Successive step change sorption experiments were carried out at two film thicknesses at 120°C in the pressure range of 0-402 mm Hg. All sorption runs exhibited a maximum in the reduced sorption curve. The fractional amount of overshoot decreased as the final pressure or weight fraction of the experiment increased and as the sample thickness increased. The overshoot in the sorption curves were caused by structural rearrangements produced by relaxation of polymer chains. None of the runs exhibited superposition of the sorption curves for two different thicknesses. However superposition was approached as the final concentration of the experiment increased.

Non-Fickian diffusion through polymer films was studied by Bum-Jong and Parrish (1985). A Cahn electrobalance was used to measure the increase in weight of a film of K-resin suspended in a large chamber of cyclohexane at 323K. The rapid uptake at short times obeyed Fickian diffusion as verified by the initial linear section of the sorption curves. After this initial period there was a slower but sustained sorption that was non-Fickian. The first stage took less time. This suggested that Fickian diffusion rapidly formed uniform cyclohexane concentration throughout the film. The second stage of slower sustained sorption suggested the adsorption of cyclohexane on the immobile sites in the polymer.

Iwai et al. (1987) measured the diffusion coefficients for three molten polystyrene-hydrocarbon systems using a quartz spring sorption apparatus in the temperature range of 130-175^{o}C. The mass fraction of the hydrocarbons ranged from 0 to 0.15. The hydrocarbons studied were m-xylene, n-octane, and n-nonane. Nunez et al. (1991) studied the sorption and diffusion of benzene in miscible blends of poly(vinyl acetate) and poly(methyl acrylate). The amount of benzene vapor absorbed by the polymer was monitored by an electrobalance. The sorption of benzene vapor into these blends was measured at a temperature above the glass transition temperatures of the pure polymers and found to obey Fickian diffusion. The mutual diffusion coefficients were estimated from the initial slopes of the sorption curves.

Moylan et al.(1991) reported the solubilities and diffusion coefficients of water vapor in four different polyimides at 22^{o}C. They used a piezoelectric quartz crystal microbalance system. Diffusion was found to be Fickian.

Doong and Ho (1992) obtained the diffusivities of a series of aromatic hydrocarbons in semicrystalline polyethylene. They used a gravimetric sorption technique with a flow system capable of a wide range of vapor pressures, and temperatures. The effect of penetrant concentration and temperature on diffusivities was investigated. A Cahn 2000 microbalance was used to measure the weight change. The diffusivities all increased with increasing penetrant concentrations and temperature. The concentration dependence appeared to become stronger with decreasing temperature or penetrant size in the order of prehnitene, n-butylbenzene, mesitylene, n-propylbenzene, toluene and benzene. The diffusivities decreased with increasing penetrant size.

CHAPTER III

THE PIEZOELECTRIC EFFECT AND ITS APPLICATION TO THE MICROBALANCE TECHNIQUE

In 1880, Pierre and Jacques Curie first observed that a pressure exerted on a small piece of quartz caused an electric potential between deformed surfaces and that physical movements of the crystal are caused by the application of voltage. This property is possible only for ionic crystalline solids that crystallize in structures lacking a center of inversion. Only materials belonging to 20 types of crystals which do not have a center of symmetry can produce this effect. The piezoelectric effect can be accounted for solely by crystal symmetry. The orientation of the quartz crystal plate with respect to the crystallographic axes was observed to have an important effect on the resonance frequency.

The present theoretical foundation for the use of the quartz crystal as a microbalance is based on the work by Lord Rayliegh. He showed that a small change in the inertia of a mechanically vibrating system perturbs the resonant frequency of the crystal. In the 1920s, Cady demonstrated the use of the inverse piezoelectric effect in the construction of a very stable oscillatory circuit. Mason demonstrated the use of the quartz crystal in ultrasonics. The shear elasticity and viscosity of liquids were measured at ultrasonic frequencies. Warner and Stockbridge were among the first to identify the important parameters in the use of a quartz crystal for mass measurement purposes. They identified the promise of an AT-cut crystal vibrating in a thickness-shear mode. In 1961 Stockbridge and Warner designed and constructed an ultrahigh vacuum system and frequency measurement and control circuitry for their quartz crystal microbalance. They showed that crystals without electrodes at the active center could tolerate vacuum bakeouts to 300^{o}C and that frequency measurements corresponding to a mass sensitivity to 10 pg/cm^{2} were possible (Czanderna and Lu, 1984).

King(1969a) described the use of the quartz crystal for a variety of applications. The paper describes the basic principle involved in the operation of the quartz crystal microbalance. King has explained how quartz crystals can be used as sorption detectors of water. He also explains the use of quartz crystals in gas chromatography.

King (1969b) explains how to prepare the crystals and discusses the use of quartz crystals in research on polymers and air pollution. In the case of polymer research, King says the crystal can be used to measure the vapor solubilities of plastics. He explains how the data obtained can be used to find the glass transition temperatures of the films coated on the crystals. He also says that good temperature control is important in these type of experiments. Some of the applications that are mentioned in the case of air pollution are the measurements of sulfide and carbonyl concentration. The quartz crystal can also be used to measure the content of residues in water. It can also be used in the analysis of hydrogen and hydrocarbons.

Chih-shun Lu (1974) in his paper on mass determination with piezoelectric quartz crystal resonators discusses the relation between the mass deposited on the quartz crystal and the change in frequency occurring due to it. He discusses various theories that had been put forward until then to explain the relation. He talks about Sauerbrey's observation that the shift in the resonant frequency for a small mass uniformly deposited on the crystal is linear and says that this is restricted to small loads. For a 5-MHz AT-cut quartz crystal, the error is less than 2% for a total mass load of less than 2 x 10^{-3}g/cm^2. He gives an equation relating the resonant frequency of the composite resonators and the acoustic impedance of the deposited material. The theoretical predictions from this equation have been compared to experimental data and have been found to be in good agreement, thus proving that quartz crystal resonators can be used for measuring large deposited masses with remarkable accuracy by using the proper formula. The results show that the mass-frequency relation derived is valid for a mass load of 50 x 10^{-3}g/cm^2 and for crystals with resonant frequencies of 4-6 MHz.

Bonner and Cheng (1975) use the piezoelectric crystal sorption device first developed by King to develop a new technique to determine the solubilities of gases in polymers at high temperatures and pressures. In this apparatus, gas from the source is passed over the polymer coated crystal (10 MHz) after passing it through a saturation column. The saturation column helps to bring the temperature of the gas to the temperature of the chamber housing the crystal. They observed that the frequency of the crystal increases as pressure increases and decreases as the temperature increases above room temperature. They studied the system nitrogen/low-density polyethylene at 125^{o}C over a pressure range of 0 to 1700 psig. Their experimental apparatus however had a pressure limitation.

Mulder (1984) built a simple piezoelectric microbalance based on a vibrating quartz wire. This microbalance is based on the mass dependence of the resonance of the quartz wire from which loads are suspended. He has discussed the construction, sensitivity, temperature dependence, operating temperatures and effect of electrostatic charging in the paper.

In order to test the of use of solid polymeric materials as desiccants, Czanderna and Thomas (1987) assembled a quartz crystal microbalance apparatus to study the water sorption of polymeric materials with thickness ranging from 0.1 to 100 μm. They use an experimental setup in which as many as five different polymer coated quartz crystals can be used simultaneously. They present data for three polymers: polyacrylamide, polyacrylic acid and poly(vinyl pyrrolidone) at 22°C. This system is advantageous as five different polymers of five different thicknesses can be studied simultaneously. The quartz crystal microbalance is sensitive enough to measure submonolayer adsorption of pure vapors and gases or their mixtures. Care must however be taken that the polymers must adhere to the gold surface.

Piezoelectric quartz crystal microbalance was also used successfully to measure the diffusion coefficient of water in 12-tungstophoric acid catalyst (Utada et al., 1991). In this study, the change in the mass of the hetropolyacid catalyst due to sorption/desorption of water. The values of the diffusion coefficients obtained were found to be of a reasonable order of magnitude.

The quartz crystal microbalance has also found wide ranging applications in the field of electrochemistry (Deakin and Buttry, 1989) and surface chemistry (Worthy, 1989). The microbalance can also be used in mass measurements associated with chemical and biological sensors and doping reactions of conducting polymers (Ward and Buttry 1990).

Application of the Piezoelectric Effect to the Quartz Crystal Microbalance

A thin piezoelectric quartz crystal was used in the present work as a microbalance. The microbalance can be excited easily by an oscillatory electrical signal. A device to measure the frequency of vibration can be coupled to the electrical circuit without significantly disturbing either the mechanical or electrical oscillation. The piezoelectric quartz crystal has a sharply defined resonant frequency at a specific crystallographic orientation and hence the frequency of vibration can be measured precisely. The crystal has the required mass sensitivity (i.e. the mass induced changes in the resonant frequency are larger than the instability of the resonant frequency). The changes in the resonant frequency due to other disturbances like a magnetic field are small in comparison with those caused due to mass change. The quartz crystal is chemically stable and small in size.

A piezoelectric quartz crystal resonator is a precisely cut slab from a natural or synthetic single crystal of quartz. When an external electric field is applied to a piezoelectric material external mechanical stresses are produced. Similarly, when there is a change in mass on the crystal, a mechanical stress is induced which causes a change in its vibrating frequency that can be measured.

The piezoelectric quartz crystal can have many modes of resonance - longitudinal mode, lateral mode, and torsional mode. Usually a quartz crystal that oscillates in only one principle mode, suppressing all unwanted modes is used. This can be done by cutting the crystal at a specific crystallographic orientation. The mode of vibration which is most sensitive to the addition of mass is the high frequency thickness shear mode. All unwanted modes can be sufficiently suppressed and separated from the principle shear mode. To make a quartz crystal plate oscillate in the thickness shear mode, the plate must be cut either in the AT-cut or the BT-cut which belongs to the rotated Y family of cuts. An advantage with the AT-cut quartz crystal is that the resonant frequency is rather insensitive to temperature changes in the region of $0^{o}C$ to $85^{o}C$.

Frequency - Mass Relation for Small Mass Loads

The following development of the frequency-mass relationship is adopted from "Applications of the Piezoelectric Quartz Crystal Microbalance" (Lu and Czanderna, 1984). The feasibility of using piezoelectric quartz resonators as quantitative mass measuring devices was first explored by Sauebrey. For a quartz crystal plate to oscillate in the fundamental thickness shear mode the following equation should be satisfied

$$t_q = \lambda_q / 2 \qquad \text{(III-1)}$$

where t_q = thickness of the plate

λ_q = wavelength of shear mode elastic wave in the thickness direction

In terms of the resonant frequency f_q and shear wave velocity v_q, Equation (III-1) can be written as

$$f_q t_q = v_q/2 \qquad \text{(III-2)}$$

$$\lambda_q f_q = v_q \qquad \text{(III-3)}$$

From Equation (III-2) the resonant frequency shift df_q caused by an infinitesimal change in the crystal thickness dt_q is found to be

$$df_q/f_q = -dt_q/t_q \qquad \text{(III-4)}$$

The negative sign indicates that an increase in the thickness of the quartz crystal plate causes a decrease in its resonant frequency.

In terms of the quartz crystal mass m_q and its mass change dm_q

$$df_q / f_q = -dm_q / m_q \qquad \text{(III-5)}$$

Sauerbrey made the assumption that for a small mass change, the addition of foreign mass can be treated as equivalent mass change of the quartz crystal itself. Hence Equation (III-5) becomes

$$df_q / f_q = -dm / m_q \qquad \text{(III-6)}$$

dm = infinitesimal amount of foreign mass uniformly distributed over the crystal surface.

On extension of the validity of the assumption to an arbitrary but small mass such as mass of a thin film Equation (III-6) can be written as

$$(f_c - f_q) / f_q = - m_f / m_q \qquad \text{(III-7)}$$

m_f = mass of a thin film

f_c = resonant frequency of quartz crystal with the deposited material.

For materials of uniform spatial density the areal density is equivalent to the product of the thickness and density hence

$$m_f = t_f \rho_f \qquad \text{(III-8)}$$

$$m_q = t_q \rho_q \qquad \text{(III-9)}$$

where m_f and m_q are the areal densities defined as mass per unit area for the deposited film and quartz crystal, respectively.

On substituting Equations (III-1) and (III-9) into (III-5) we get

$$m_f = \frac{\left(f_c - f_q\right)\rho_q v_q}{2 f_q^2} \qquad \text{(III-10)}$$

ρ_f = density of the film

ρ_q = density of quartz crystal

If the film density is known, on substitution of Equation (III-8) into Equation (III-14) we get

$$\rho_f t_f = \frac{-(f_c - f_q)\rho_q v_q}{2f_q^2} \qquad \text{(III-11)}$$

This equation can be employed to determine the film thickness.

Equation (III-10) can be simply written as

$$\Delta f = -C_f m_f \qquad \text{(III-12)}$$

where the frequency shift is $\Delta f = f_c - f_q$.

This demonstrates the linear relationship between the frequency change and mass change.

CHAPTER IV

EXPERIMENTAL APPARATUS AND PROCEDURE

Description of the Apparatus

The objective of this work was to design and construct an experimental apparatus using a piezoelectric quartz crystal microbalance to measure the sorption of a penetrant into a polymer film. The polymer film was subjected to a pure penetrant atmosphere with an extremely low level of contaminants. The experiment was conducted in a high vacuum chamber so that minimal contamination was present. The chamber was required to have the following characteristics:

1. One opening to insert the crystal holder.
2. One opening to introduce the penetrant.
3. One opening to connect the vacuum generation system.
4. One opening to introduce a temperature measurement device in the chamber.
5. One opening to introduce a pressure measurement device into the chamber.
6. One viewport.

A high vacuum six-way cross was obtained from the Kurt J. Lesker Company

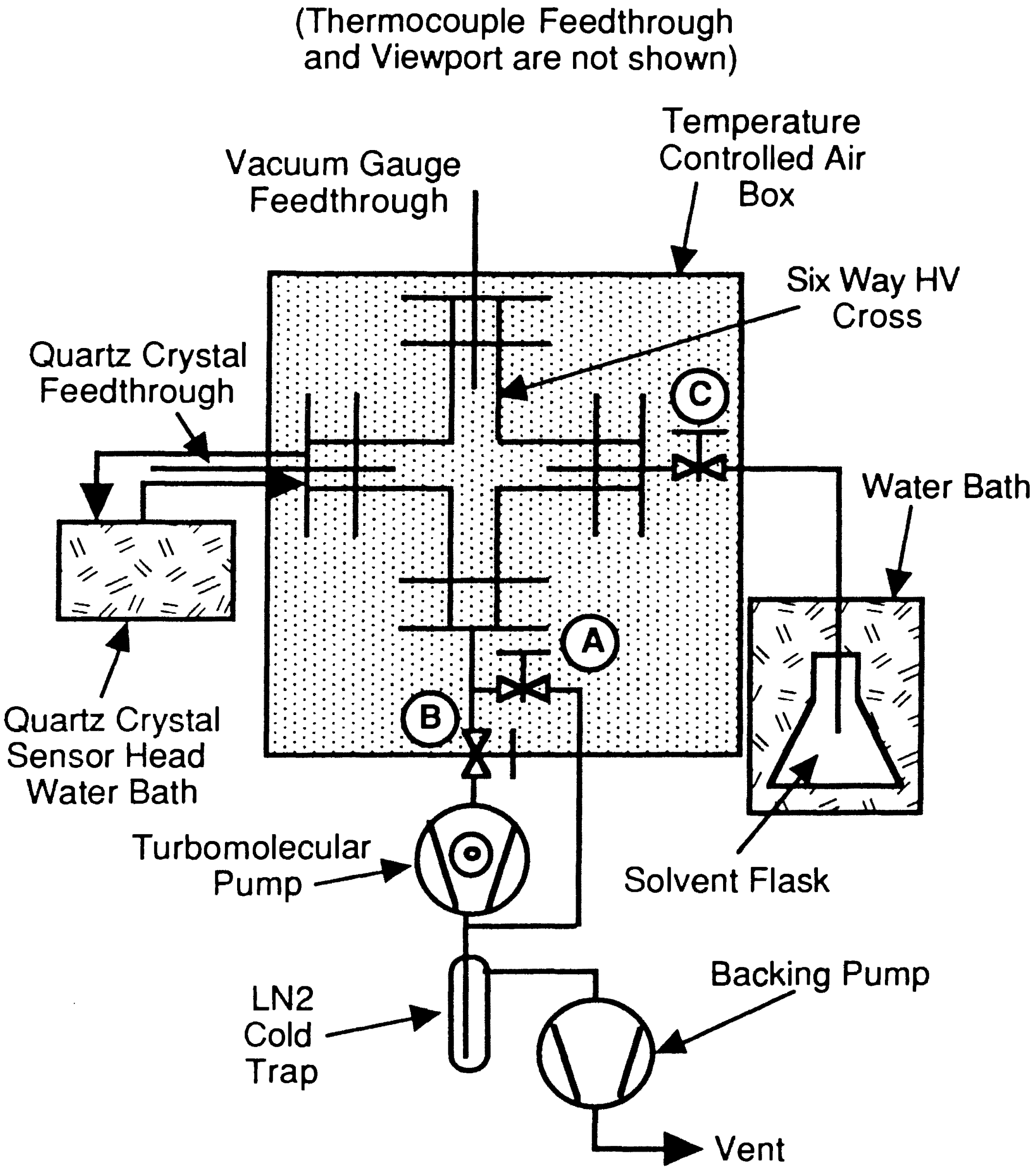

Figure 2 Schematic of the Apparatus

for use as the experimental chamber. The six-way cross is a commercially available component fabricated from 304 stainless steel and uses knife edge flanges and copper gaskets to achieve positive sealing. Copper gaskets have been used as they provide metal to metal contact and hence are better suited for generating clean, high vacuum. Rubber gaskets or connecting devices have been avoided in and around the six way cross to eliminate any possibility of contaminating the penetrant atmosphere in the chamber. The chamber is operable from 10^{-11} torr to slight positive pressures and over a temperature range of -196°C to +500°C. Three flanges of the six-way cross are rotatable and three are fixed. The flange diameter is 6 inches and the outer tube diameter is 4 inches.

A Leybold Inficon standard crystal holder (Model # 750-207-G1) was used as the sensor. This sensor is made of 304 type stainless steel, and the springs used in this sensor are gold plated Be-Cu. The crystal holder has a water circulating facility. The maximum operable temperature without cooling water circulation is 130°C. The maximum operating isothermal environment temperature with minimum cooling water flow is 400°C. The crystal has a diameter of 0.550 inches and the crystal can be changed easily.

A quartz crystal deposition process controller manufactured by Leybold Inficon (model XTC/2) was used to monitor the sorption of the penetrant by the polymer. The liquid crystal display of the XTC/2 keeps the operator continuously informed of pertinent deposition data such as rate, thickness, and elapsed time. It also flashes special operational messages such as "stop", "crystal fail", and hence, reduces operator uncertainty, thus minimizing the possibility of costly errors. Though the XTC/2 has many other applications, it was used only as a deposition monitor in this experiment.

The polymer film coated on the crystal had to be maintained at an accurately controlled temperature. This was accomplished by using a Lauda heating circulator manufactured by Brinkmann Instruments Inc. (Model MT). This circulator is connected to the cooling water connection provided in the crystal holder. The water was allowed to circulate for a few hours before starting the experiment to bring the polymer film to the desired temperature. Water was also circulated during the experimental run to maintain a constant temperature of the polymer film.

Since the chamber had to be contaminant free, the system was evacuated to a very high vacuum using two pumps. A rotary vane pump was used as a roughing pump and a turbomolecular pump was used to reach the high vacuum range. For the roughing pump, a Leybold TRIVAC A rotary vane pump (Model 4A) which can reach vacuums upto 10^{-2} torr was used. This is an oil-sealed rotary vane pump designed for operation in rough to medium vacuum applications. A liquid nitrogen trap was placed between the pumps and the vacuum chamber.

For creation of high vacuum, a Leybold Turbovac 50 turbomolecular pump which can reach vacuums from 10^{-2} torr to 10^{-5} torr was used. A Turbotronic NT 50 solid state frequency converter manufactured by Leybold Inficon is required to power the motor in the Turbovac 50. The main frequency of 50/60 Hz is converted to the specific operating frequency of the Turbovac motor. The motor temperature of the turbovac is also monitored by the Turbotronic NT 50 and in case of unpermissibly high temperatures, it switches off the voltage and signals a failure to the operator. Under the operating conditions in the experiment, no extra cooling of the turbomolecular pump was required. Since the quartz crystal microbalance is very sensitive to vibrations, a metal bellows was placed between the turbomolecular pump and the chamber.

A Tee joint was used to connect the bellows to a gate valve (valve B) and a right angle valve (valve A). Valve B was connected to the turbomolecular pump and valve A was connected to the rotary vane pump through the liquid nitrogen trap. The vent of the turbomolecular pump was also connected to the liquid nitrogen trap. Valve B was necessary to connect the vacuum chamber to either the turbomolecular pump or to the roughing pump. This arrangement was required so that rough vacuum could be created by bypassing the turbomolecular pump. This was necessary so that the vapors did not enter the turbomolecular pump, during roughing. A Leybold Inficon SG series manually activated valve with Viton O-ring gate seals and bellows sealed shaft was used as valve B. This valve has an operating pressure range of 10^{-9} to 760 torr and is bakable up to $200^{o}C$. Viton gaskets were used in the foreline of the turbomolecular pump as metal gaskets were not appropriate. The manual right angle valve used was manufactured by Huntington laboratories (model EV 150).

The liquid nitrogen trap was used in the system for two reasons. Since a rotary vane pump was being used, there was a possibility that some oil vapors might backstream to the chamber. Also, the oil in the rotary vane pump can easily be contaminated by penetrant vapors when the chamber is being evacuated. The pump oil would then have to be changed frequently. The liquid nitrogen trap eliminates these difficulties. The liquid nitrogen trap used was purchased from the Kurt J. Lesker Company (Model LNF1000).

The third opening of the six-way cross was used to introduce the penetrant into the chamber via a toggle valve (valve C, Kurt J. Lesker Company model VZCRT 'T' valve) and appropriate reducing flanges. This valve can maintain a vacuum down to 10^{-12} torr and has a small dead volume of 0.1 ml. The toggle valve was used to control the flow of the penetrant to the chamber. The valve was connected to a flask containing the penetrant using 1/4 inch stainless steel tubing. A needle valve was installed in the piping to isolate the flask and vent the system to the atmosphere.

The flask containing the penetrant was kept in a water bath heated with a constant temperature immersion circulator (Fisher Scientific Model 70). This was used to keep the penetrant at the desired temperature. The temperature was measured using a mercury thermometer provided with the immersion circulator.

The fourth opening of the six-way cross was used to connect the two pressure gauges to the chamber. A Pirani gauge (Leybold Model PG3) and a hot cathode ionization gauge (Leybold model IG3) were used to measure low and high vacuum, respectively. There is one basic controller chassis for each gauge and each controller supports a primary sensing technology. The primary sensor used for the Pirani gauge was manufactured by Leybold (Model TR901). The primary sensor used in the hot cathode ionization gauge was a standard Bayard-Alpert type glass tubulated sensor. The Pirani gauge has a pressure range of 1×10^{-4} to $1 \times 10^{+3}$torr. The hot cathode ionization gauge has a range of 1×10^{-10} to 1×10^{-2} torr. To prevent debris from entering the gauges and to provide the best possible accuracy, the gauges were installed vertically with their inlet pointing downwards.

The fifth opening of the six-way cross was used to introduce a resistance temperature device (RTD) into the chamber to measure the temperature inside the chamber. The RTD has been connected to a temperature controller unit which controls the temperature inside the chamber. An LFE Instruments (Model 2000) temperature controller was used. Heating tapes manufactured by Omega Technologies were used to heat the chamber. They were taped around four openings of the six way cross. This was done to ensure uniform heating inside the chamber. The heating tapes were also connected to the temperature controller unit which activated and deactivated them as necessary. The heating tapes used were moisture and chemical resistant.

The last opening of the six-way cross was used as a viewport permitting observation of the diffusion process. The viewport was necessary to observe if any condensation of the penetrant vapor had occurred in the chamber. Condensation of the penetrant inside the chamber is undesirable as it would adversely affect the working of the quartz crystal microbalance.

As the experimentation progressed, the results indicated that along with the polymer film being maintained at a steady temperature, the entire vacuum system had to be maintained at the same constant temperature to eliminate formation of 'cold spots' in some parts of the system which are at a lower temperature. Due to these cold spots, solvent would condense in the parts at the lower temperature leading to erroneous results. The condensation of the solvent in some parts of the system also made creation and maintenance of vacuum in the system difficult.

Uniform heating was accomplished by building a thermal box enclosing the system. The thermal box was built using half inch thick plywood lined with flexible insulating material which could withstand temperatures up to 150°C. A 475 watt, 4 amp, Omega heating element was used to heat the thermal box. The heating element was mounted at the outlet of a circulating fan which was used to circulate the air within the enclosed space. The circulating fan was a Dayton fan operable upto 200°C. An Omega microprocessor controller (model CN 9000) was used to control the temperature to within 0.1°C. The controller was connected to a three wire RTD probe (model RTD 805) which was mounted on the frame of the thermal box.

The deposition monitor has been interfaced to a computer using an RS232 connection. A computer program that records data at regular intervals during the experiment has been written. A listing of the computer code is provided in Appendix D.

Coating of the Quartz Crystal

The polymer film is solution cast onto the crystal. A polymer film is cast from a solution with a known concentration onto an area of the quartz crystal exposed by a teflon washer. Since a known volume of the solution is used, the thickness of the film can be calculated. The film wa s assumed to be of uniform thickness.

CHAPTER V

RESULTS AND DISCUSSION

The main goals of this work were to develop and test an experimental technique to study the sorption of penetrants into polymers. An apparatus using a piezoelectric quartz crystal microbalance was designed and constructed. Four systems were studied to test the apparatus: polystyrene-acetone, polystyrene-water, poly(vinyl methyl ether)-water and poly(vinyl acetate)-toluene. The rate at which the penetrant was sorbed by the polymer was measured by recording the change in the frequency of the quartz crystal as a function of time. The data can be reduced to a sorption curve and diffusion coefficients can be calculated. The results obtained in this study are discussed in this chapter.

Analysis of the Quartz Crystal Microbalance Data

The mutual diffusion coefficient of a penetrant-polymer system determined from sorption data typically relies on the initial slope method (Crank, 1975). With this method, the slope of the initial portion of the Fickian sorption curve is measured and used to calculate the diffusion coefficient. The average diffusion coefficient is calculated from

$$\bar{D} = \frac{\pi}{4} R^2 \qquad \text{(V-1)}$$

where

$$R = \frac{d\left(\frac{M(t)}{M(\infty)}\right)}{d\left(\frac{t}{l^2}\right)^{\frac{1}{2}}} \qquad \text{(V-2)}$$

where l = thickness of the polymer film

M(t) = mass of the solvent sorbed by the polymer at time t

M(∞) = mass of the solvent sorbed by the polymer at equilibrium.

A detailed derivation of equation (V-1) is given by Vrentas and Duda (1968). The slope of the initial portion of the sorption curve has been found using Microsoft Excel software. After determining the slope of the initial 60% of the sorption curve and the thickness of the polymer film, the average diffusion coefficient can be found using Equation (V-1), (Duda and Zelinski, 1992).

For the quartz crystal microbalance to be useful as a measurement device for diffusivities, the frequencies obtained from the quartz crystal microbalance must be related to the appropriate mass quantities in Equation (V-2). At low mass loadings, the frequency change of the piezoelectric quartz crystal is proportional to the change of mass on the crystal. Therefore, the ratio of the mass at time t to the mass at infinite time can be found from:

$$\frac{M(t)}{M(\infty)} = \frac{C(f_3 - f_2)}{C(f_4 - f_2)} = \frac{(f_3 - f_2)}{(f_4 - f_2)} \qquad \text{(V-3)}$$

C = proportionality constant

f_1 = frequency of the bare crystal, Hz

f_2 = frequency of the crystal with only the polymer film coating, Hz

f_3 = frequency of the crystal at any time t after the start of the experiment, Hz

f_4 = frequency of the crystal at equilibrium, Hz

The constant of proportionality, C, cancels so that the ratio can be obtained directly from the frequencies and it is not necessary to know the value of C.

The weight fraction of the solvent sorbed by the polymer film can be calculated using the formula

$$\omega = \frac{(f_3 - f_2)}{(f_3 - f_1)} \tag{V-4}$$

ω = Weight fraction of the solvent sorbed by the polymer film

If the weight fraction is found to increase as the diffusion coefficient increases then the average weight fraction can be calculated to be

$$\bar{\omega} = \omega(initial) + (0.7)[\omega(final) - \omega(initial)] \tag{V-5}$$

$\bar{\omega}$ = Average weight fraction of the solvent sorbed by the polymer film.

Equation (V-5) is based on an analysis of the sorption experiment by Duda and Vrentas (1977).

Sorption Experiments Conducted Using the Quartz Crystal Microbalance

In the study of the piezoelectric quartz crystal microbalance, four systems were studied to develop and validate the technique. The purpose of this study was to verify the capabilities of the instrument. The polymer-solvent systems were chosen for operational convenience and not for a specific application. During the course of the study, as further experience was acquired, several refinements were made to the experimental apparatus. The first three systems polystyrene-acetone, polystyrene-water, poly(vinyl methyl ether)-water, helped identify the shortcomings of the apparatus and modify the equipment accordingly.

The first system studied to test the apparatus was the polystyrene-acetone system. The polystyrene-acetone system shows anomalous behavior at room temperature as was expected (Duda and Vrentas, 1970). Five runs were conducted on this system. The reduced sorption curves obtained from these runs did not show the characteristics described in the literature and were not reproducible.

While evacuating the chamber after each run, solvent was removed via the turbomolecular pump and the roughing pump. This damaged the turbomolecular pump since the acetone dissolved the grease on the bearings of the turbomolecular pump. Hence, the equipment had to be redesigned such that the chamber could be evacuated by the roughing pump while bypassing the turbomolecular pump thus enabling the equipment to handle solvents such as acetone.

Due to the problems encountered while working with acetone, the system was changed to polystyrene-water. This system has been reported to show Fickian behavior (Duda and Vrentas, 1970). Nine runs were conducted on the system. The results obtained from these runs showed that the initial part of the reduced sorption curve followed Fickian diffusion, but the maximum amount of solvent sorbed was not constant. Again, these results were not consistent with those reported in literature. The incorrect results were attributed to two probable reasons:

1. The experiments were being conducted very much below the glass transition temperature of the polymer.
2. At this point the equipment did not have the capability to maintain the polymer film at a constant temperature and hence the experiments had been carried out at ambient temperature which changed during the course

of the experiment. This change in temperature could have been reflected in the results of the experimental runs.

To eliminate these problems, the system was changed to poly(vinyl methyl ether)-water as poly(vinyl methyl ether) has a glass transition temperature of -37°C and heating tape was wound around each of the arms of the six way cross to maintain the chamber at a constant temperature. Since the glass transition temperature of poly(vinyl methyl ether) in the pure state is low, at room temperature the polymer is above the glass transition temperature and all polymer-solvent systems are supposed to show Fickian diffusion in the region above the glass transition temperature (Crank and Park, 1968).

The experiments were performed by maintaining the temperature of the polymer film at 45°C. The water was maintained at room temperature. A comparative study of the first five runs is shown in Figure 3. The results of these runs were reproducible in the initial portion of the sorption curve, but the maximum amount of solvent sorbed did not remain constant. The shape of the sorption curve was similar in each of these runs. A total of five runs were made on this system. The reason that the amount of solvent sorbed does not stay constant at equilibrium was most likely due to the lack of temperature control of the solvent bath. Thus temperature control was found to be a very important factor in this experiment.

Since the results obtained from the poly(vinyl methyl ether)-water system were reproducible and the noise in the equilibrium amount of solvent sorbed was attributed to inadequate temperature control, we felt we had sufficient understanding of the equipment to rectify this fault and validate the equipment by

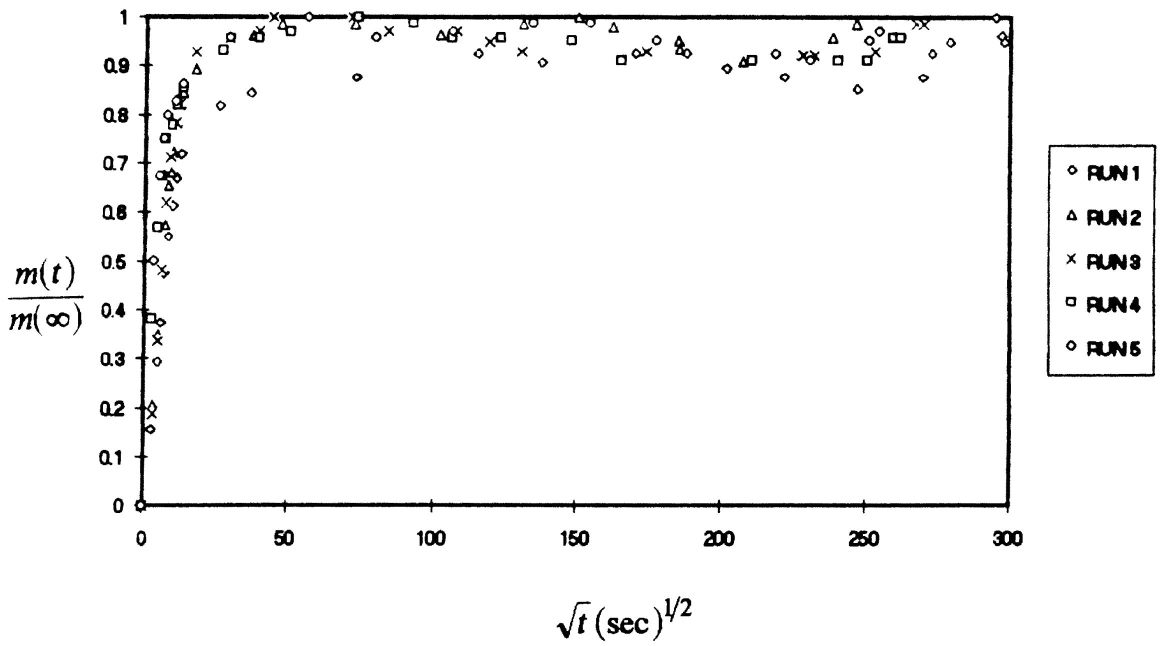

Figure 3. Sorption of Water in Poly(vinyl metyl ether) Run Nos: 1, 2, 3, 4, 5

Temperature: 45°C

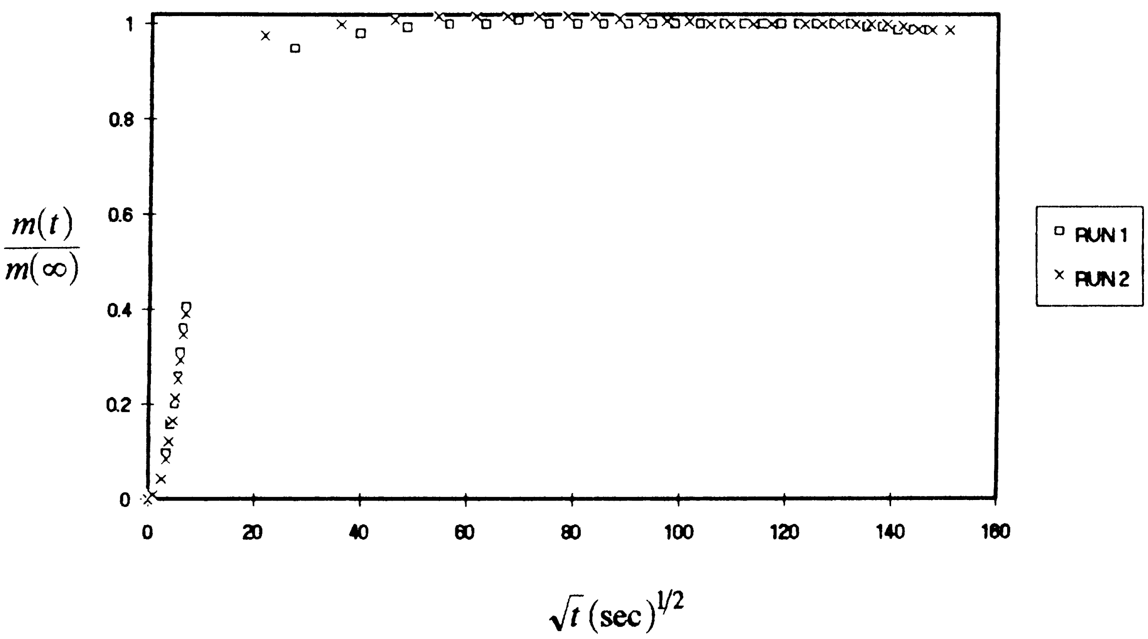

Figure 4. Sorption of Toluene on Poly(viny acetate) Run Nos. 1, 2

Temperature of Film: 80°C
Temperature of Solvent Bath: 40°C

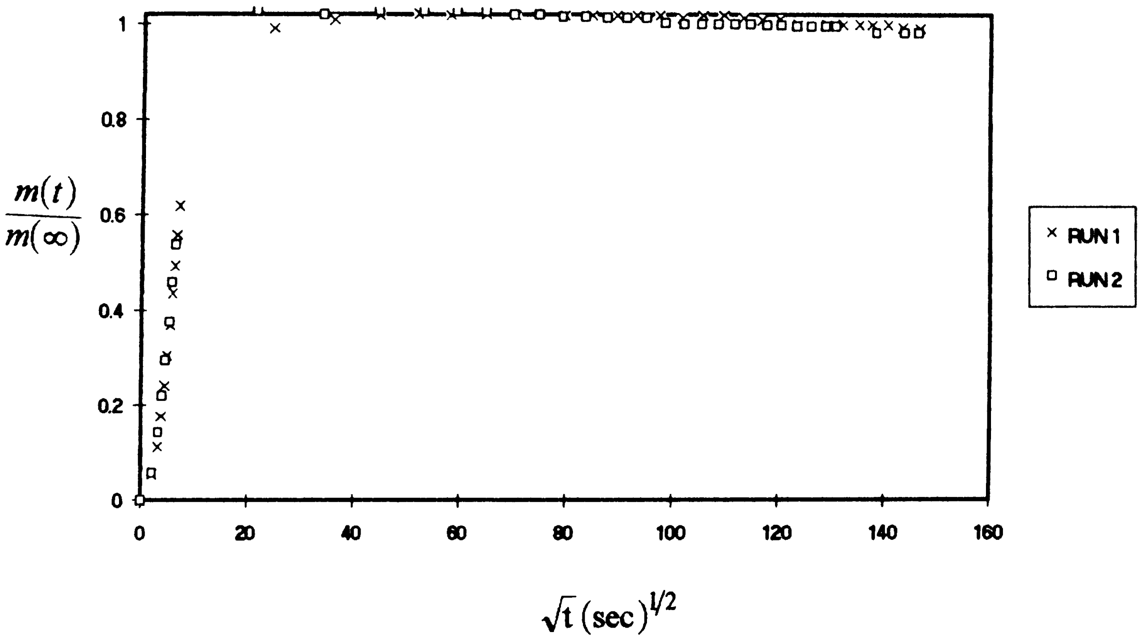

Figure 5. Sorption of Toluene on Poly(vinyl acetate) Run Nos. 1, 2

Temperature of Film: 80°C
Temperature of Solvent Bath: 50°C

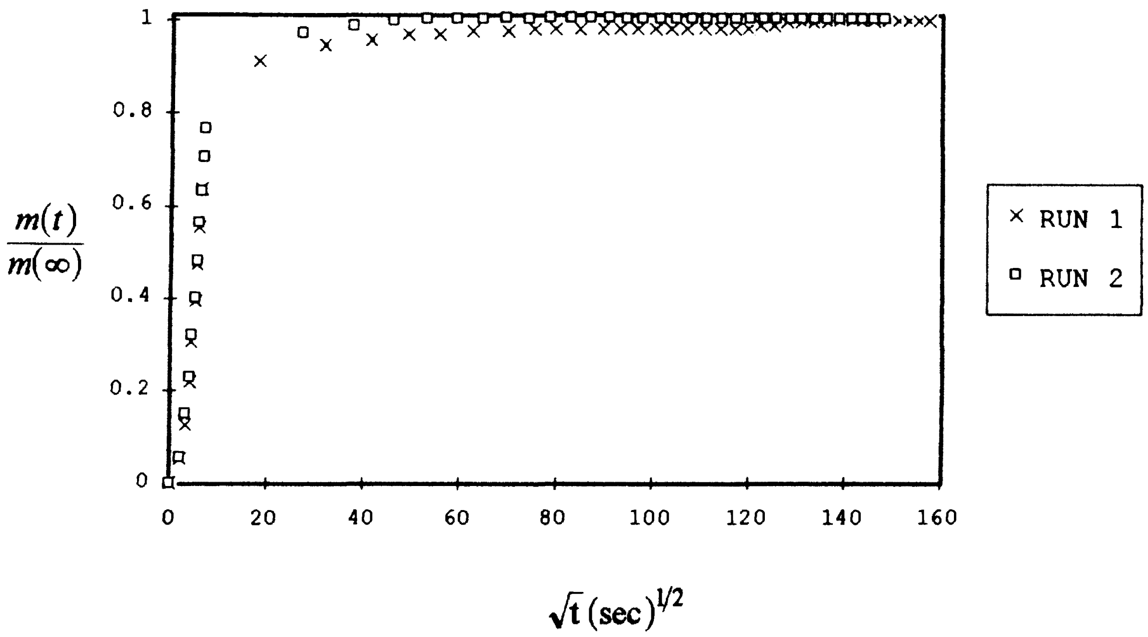

Figure 6. Sorption of Tolene on Poly(vinyl acetate) Run Nos. 1, 2

Temperature of Film: 80°C
Temperature of Solvent Bath: 55°C

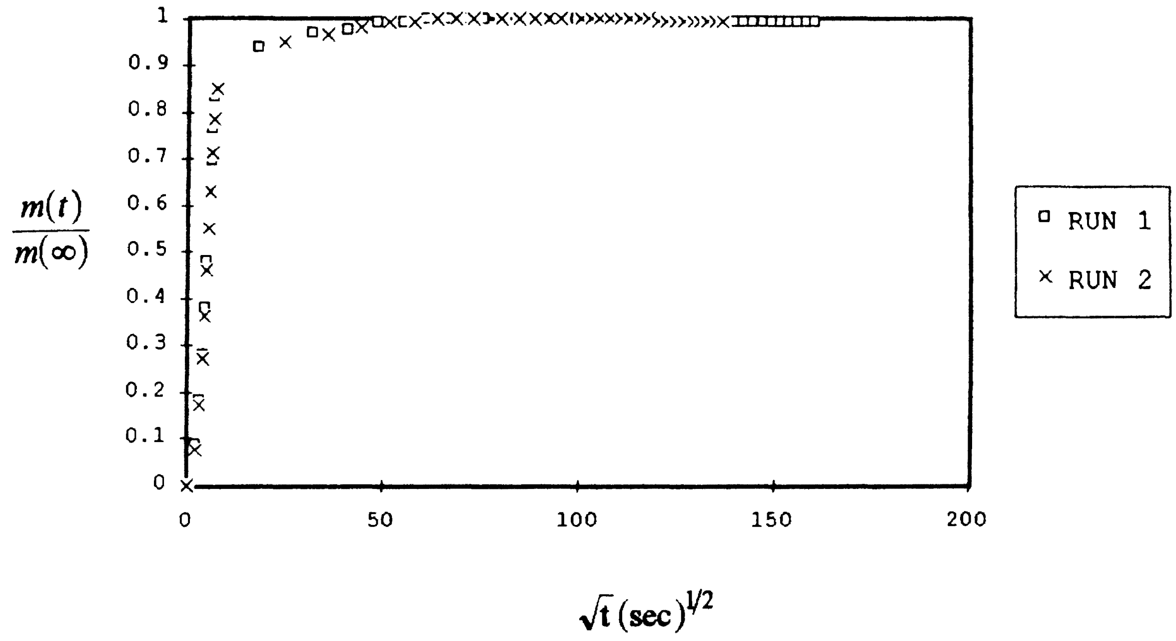

Figure 7. Sorption of Toluene on Poly(vinyl acetate) Run Nos. 1, 2

Temperature of Film: 80°C
Temperature of Solvent Bath: 65°C

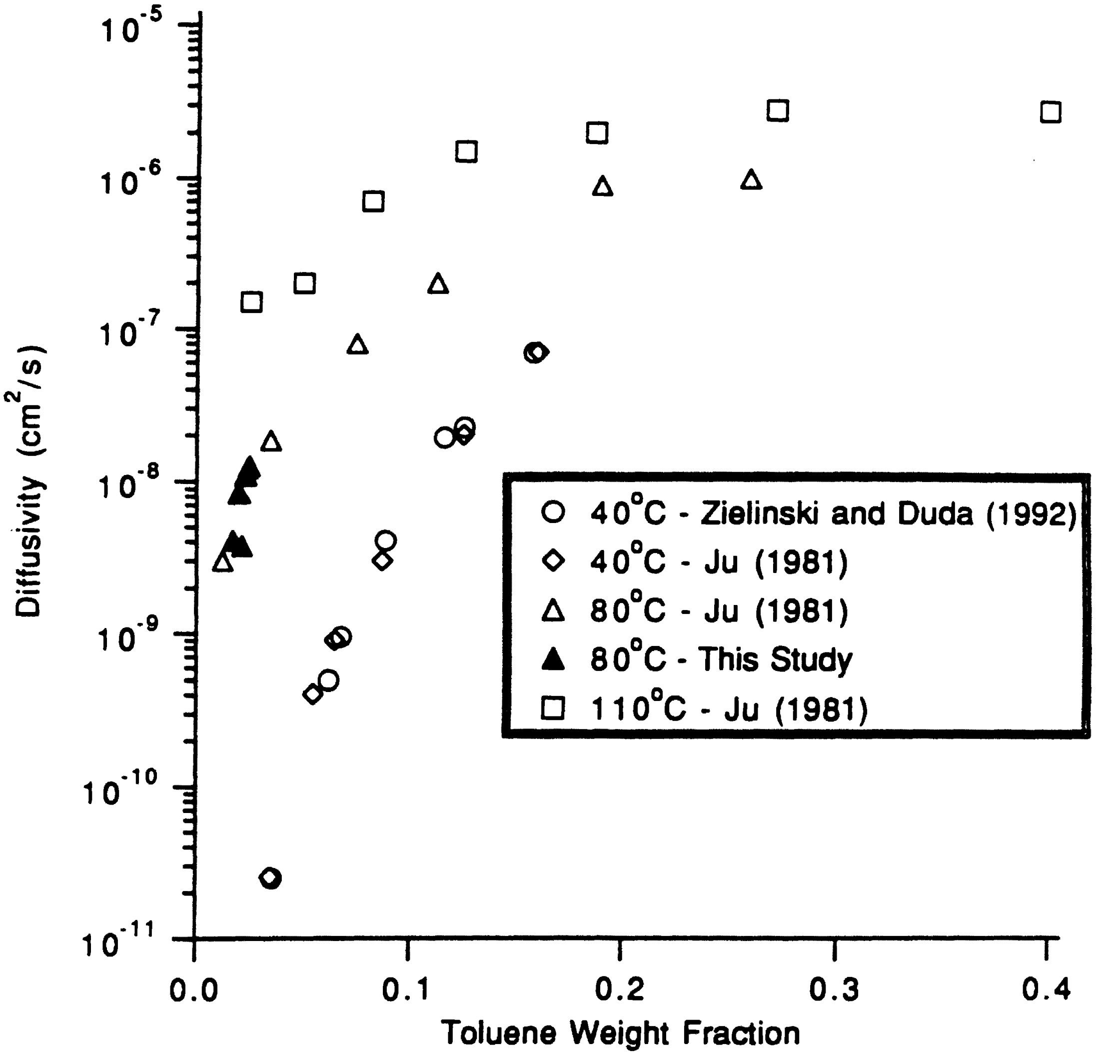

Figure 8. Comparison of the Diffusion Coefficients Obtained Using the Quartz Crystal Microbalance and the Quartz Spring Balance

TABLE II

WEIGHT FRACTIONS AND CORRESPONDING DIFFUSION COEFFICIENTS FOR POLY(VINYL ACETATE)-TOLUENE

Temperature of Solvent bath	Weight Fraction	Diffusion coefficient cm^2/sec
40^o C	0.017	4.06E-09
	0.022	3.72E-09
50^o C	0.020	8.23E-09
	0.021	8.32E-09
55^o C	0.024	1.09E-08
	0.023	1.08E-08
65^o C	0.025	1.26E-08
	0.024	1.21E-08

reproducing quantitatively results reported in the literature. The poly(vinyl acetate)-toluene was chosen for this purpose as it had been extensively studied by Duda and coworkers.

Poly(vinyl acetate)-Toluene System

Experiments were conducted by maintaining the temperature of the equipment at 80^oC. This was achieved by constructing a thermal box enclosing the equipment. The temperature of the solvent bath was maintained at 40^oC in the first set of runs and then increased to 50^oC, 60^oC and 65^oC. The results of these runs are shown in Figures 4, 5, 6 and 7, respectively. As can be seen the value of $M(\infty)$ remains constant. The diffusion coefficients and corresponding weight fractions are given in Table 2. Figure 8 gives a comparison of the results obtained from thequartz crystal microbalance and the results obtained by Duda and Zelinski(1992). The diffusion coefficients obtained using the quartz crystal microbalance are within the range of the weight fractions obtained by Duda and Zelinski, but not identical. The diffusion coefficients from the quartz crystal microbalance are in excellent agreement with those obtained by Duda and Zelinski. These results quantitatively validate the quartz crystal microbalance as an apparatus for the measurement of diffusion coefficients for polymer solvent systems.

One failing of the diffusion coefficient data collected using the quartz crystal microbalance is that the range of weight fractions over which the data were collected is not very wide. Data could not be collected over a wider range because condensation was observed in the crystal chamber at solvent bath temperatures above 70^oC. The solution to this problem would be to get better temperature control for the system in order to reach higher solvent bath temperatures. If better temperature control is used, diffusion coefficients over a wider range of weight fractions can be obtained.

An important conclusion that can be drawn from these results is that the behavior of a polymer-solvent system is very sensitive to changes in the experimental conditions. Installation of the temperature control system was the most important factor in getting good, reproducible results for the various polymer-solvent systems. The temperature sensitivity can be interpreted in another manner since it is also possible that the microbalance and not the polymer-solvent is sensitive to changes in temperature. This will have to be studied in more detail by conducting the same experiment on another apparatus like the quartz spring balance and checking to see if the polymer-solvent system is sensitive to temperature changes.

A very important variable that has not been controlled very well is the thickness of the film. The thickness of the film is not measured very precisely. Hence we cannot state the thickness of the film and its uniformity with confidence.

CHAPTER VI

CONCLUSIONS

The following conclusions can be drawn from this study:

- A piezoelectric quartz crystal microbalance has been designed and constructed for the study of sorption of penetrants into polymers.
- Four polymer-penetrant systems were studied during the course of this work. Poor qualitative results were obtained for the polystyrene-acetone system.
- Reasonable qualitative results were obtained for the polystyrene-water and poly(vinyl methyl ether)-water system. These systems were used to gain operative knowledge of the instrument under moderate temperatures. The results have improved as modifications were made in the experimental setup.
- Diffusion coefficients were calculated for the poly(vinyl acetate)-toluene system and they have been found to be in excellent agreement with those reported by Duda and Zelinski(1992).

CHAPTER VII

RECOMMENDATIONS

The goals of this work were to setup and validate an experimental apparatus using a quartz crystal microbalance to study the sorption of penetrants into polymers. While these goals have been achieved, certain improvements in the method of conducting the experiments can improve the accuracy of the results. Also, experiments with other methods should be carried out to obtain diffusivity data. The following recommendations are made based on these points:

- A method needs to be developed to check the uniformity of the polymer film coated on the crystal. Use of a profilometer is recommended.
- Better control of the temperature of the polymer film would lead to better results. Right now the gate valve is outside the thermal box. On closing the gate valve while conducting the experiment, it becomes a part of the system and hence it should be moved inside the thermal box to eliminate a potential cold spot
- Increase the heating capacity of the thermal box to expand the temperature range of the experimental setup. This can be accomplished by introducing a heating coil in parallel with the one already present

- The polystyrene-acetone system should be studied again to obtain good quantitative results and to see if the modifications made in the apparatus make the apparatus more reliable.
- Desorption experiments should be conducted especially for systems that show Fickian behavior. This will help validate the apparatus further as results obtained from sorption and desorption experiments should be identical.

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APPENDIX A

EXPERIMENTAL DATA FOR POLY(VINYL METHYL ETHER)-WATER AND POLY(VINYL ACETATE)-TOLUENE SYSTEMS

TABLE III

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL METHYL ETHER)-WATER TEMPERATURE: 45 C
RUN NO: 1

Time (secs)	Frequency (Hz)
0.00	5958653.50
21.04	5958644.40
42.16	5958632.50
63.33	5958624.40
84.67	5958619.10
105.98	5958616.30
127.24	5958613.40
148.52	5958610.10
169.83	5958608.20
400.99	5958602.00
789.58	5958600.50
1178.13	5958599.10
1566.62	5958598.60
1955.21	5958598.10
2343.75	5958597.70
2732.27	5958597.70
3120.84	5958596.70
3509.36	5958596.20
3897.87	5958596.20
4286.44	5958596.20
4674.96	5958596.20
5063.50	5958596.20
5452.02	5958596.20
5840.59	5958595.80
6229.13	5958595.80
6617.62	5958594.80
7006.19	5958594.80
7394.70	5958594.80
7783.22	5958594.80
8171.73	5958594.80
8560.33	5958594.80
9170.94	5958594.80
9781.49	5958593.80

TABLE III (CONTINUED)

Time (Secs)	Frequency (Hz)
10391.98	5958593.80
11002.57	5958592.40
11668.57	5958592.40
12279.17	5958592.40
12889.70	5958592.40
13500.28	5958592.40
14110.80	5958592.40
14721.30	5958593.80
15331.87	5958593.80
15942.43	5958593.80
16552.98	5958593.80
17163.53	5958593.80
17774.11	5958593.80
18384.64	5958593.80
18939.66	5958592.40
19550.21	5958592.40
20160.73	5958592.40
20771.37	5958592.40
21381.89	5958592.40
21992.47	5958592.40
22602.97	5958592.40
23269.05	5958592.40

TABLE IV

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL METHYL ETHER)-WATER TEMPERATURE: 45 C
RUN NO: 2

Time (secs)	Frequency (Hz)
0.00	5958658.70
21.04	5958645.80
42.16	5958632.50
63.38	5958624.40
84.75	5958619.10
106.01	5958616.30
127.40	5958612.00
148.68	5958610.10
169.94	5958608.20
727.52	5958601.00
1550.16	5958599.10
2646.92	5958598.60
3606.57	5958598.60
4566.26	5958598.60
5525.95	5958599.10
6622.75	5958599.10
7582.36	5958600.00
8542.10	5958600.50
9501.79	5958600.00
10461.44	5958599.10
11421.07	5958599.10
12517.85	5958598.60
13477.56	5958598.60
14437.25	5958598.60
15396.93	5958598.60
16356.54	5958598.60
17316.20	5958598.10
18275.88	5958598.10
19235.57	5958598.10
20195.23	5958598.10
21155.02	5958598.10
22114.71	5958597.70
23074.40	5958598.10

TABLE IV (CONTINUED)

Time (Secs)	Frequency (Hz)
24034.08	5958598.60
24993.74	5958598.60
25953.45	5958599.10
26913.11	5958600.00
27872.77	5958600.50
28832.42	5958600.50
29792.09	5958601.00
30751.77	5958601.00

TABLE V

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL METHYL ETHER)-WATER TEMPERATURE: 45 C RUN NO: 3

Time (secs)	Frequency (Hz)
0.00	5958661.60
21.10	5958649.60
42.21	5958636.30
63.36	5958626.30
84.75	5958620.50
106.01	5958617.20
127.30	5958615.80
148.60	5958613.90
169.86	5958612.00
727.41	5958604.80
1687.07	5958602.90
2646.75	5958602.00
3606.41	5958602.00
4566.10	5958602.00
5525.76	5958602.90
6485.47	5958602.90
7445.13	5958603.90
8404.81	5958603.90
9364.47	5958603.90
10324.19	5958603.90
11420.96	5958603.90
12380.65	5958604.80
13340.33	5958604.80
14299.99	5958605.30
15259.73	5958605.30
16219.39	5958605.30
17179.05	5958605.30
18138.71	5958606.70
19098.40	5958606.70
20058.11	5958606.70
21017.90	5958606.70
21977.56	5958606.70
22937.28	5958606.70

TABLE V (CONTINUED)

Time (Secs)	Frequency (Secs)
23896.96	5958606.70
24856.59	5958606.70

TABLE VI

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL METHYL ETHER)-WATER TEMPERATURE: 45 C RUN NO: 4

Time (secs)	Frequency (Hz)
0.00	5958653.90
21.26	5958634.40
42.56	5958622.50
63.82	5958618.20
85.24	5958617.20
106.50	5958615.80
127.78	5958613.90
149.06	5958613.40
170.40	5958612.00
727.87	5958606.70
1687.56	5958603.90
2647.24	5958602.90
3606.93	5958602.00
4566.61	5958602.00
5526.27	5958602.90
6486.01	5958602.90
7445.67	5958602.90
8405.33	5958602.90
9364.99	5958603.90
10324.68	5958604.80
11284.33	5958605.30
12244.04	5958605.30
13203.70	5958605.30
14163.39	5958604.80
15123.16	5958604.80
16082.81	5958605.30
17042.47	5958605.30
18002.13	5958605.30
18961.87	5958605.30
19921.53	5958605.30
20881.25	5958605.30
21840.98	5958605.30
22800.64	5958606.70

TABLE VI (CONTINUED)

Time (secs)	Frequency (Hz)
23760.30	5958606.70
24720.04	5958607.20
25679.73	5958607.20
26776.48	5958607.20

TABLE VII

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL METHYL ETHER)-WATER TEMPERATURE: 45 C RUN NO: 5

Time (secs)	Frequency (Hz)
0.00	5958651.50
21.28	5958629.10
42.62	5958620.10
63.87	5958615.80
85.25	5958614.30
106.53	5958613.90
127.87	5958613.40
149.15	5958612.00
170.43	5958611.50
727.95	5958605.30
1687.75	5958602.00
2647.41	5958602.00
3607.07	5958602.90
4566.81	5958603.90
5526.46	5958603.90
6486.12	5958604.80
7308.71	5958604.80
8268.45	5958603.90
9228.11	5958603.90
10187.77	5958603.90
11147.43	5958603.90
12107.14	5958602.90
13066.83	5958603.90
14026.51	5958602.90
14986.20	5958602.90
15945.86	5958602.90
16905.60	5958602.90
17865.26	5958602.00
18824.92	5958602.00
19784.57	5958602.00
20744.32	5958602.90
21704.08	5958602.00
22800.86	5958602.00

TABLE VII (CONTINUED)

Time (Secs)	Frequency (Hz)
23760.55	5958602.90
24720.21	5958603.90
25679.86	5958603.90
26502.49	5958603.90

Table VIII

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL ACETATE)-TOLUENE TEMPERATURE OF FILM: 80 C TEMPERATURE OF SOLVENT BATH:40 C RUN NO: 1

Time (secs)	Frequency (Hz)
0.00	5964245.80
5.91	5964244.40
11.76	5964241.50
17.77	5964233.40
23.76	5964226.20
29.81	5964220.00
35.76	5964212.90
41.77	5964205.30
47.76	5964198.60
53.78	5964191.90
195.84	5964111.30
1018.43	5964115.60
1807.41	5964112.30
2629.97	5964110.40
3452.54	5964110.40
4275.10	5964109.40
5097.72	5964109.40
5920.28	5964110.40
6742.90	5964110.40
7565.47	5964110.40
8388.03	5964110.40
9210.60	5964110.40
10033.22	5964110.40
10855.78	5964110.40
11678.39	5964110.40
12500.96	5964110.40
13323.52	5964110.40
14146.09	5964110.40
14968.71	5964110.40
15791.38	5964110.40
16613.92	5964110.40
17436.56	5964110.40
18259.13	5964111.30

TABLE VIII (CONTINUED)

Time (Secs)	Frequency (Hz)
19081.75	5964111.30
19904.31	5964112.30
20726.93	5964112.30
21549.55	5964112.30
22372.11	5964113.20
22509.21	5964113.20

TABLE IX

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL ACETATE)-TOLUENE TEMPERATURE OF FILM: 80 C TEMPERATURE OF SOLVENT BATH:40 C RUN NO: 2

Time (secs)	Frequency (Hz)
0.00	5964256.80
0.94	5964255.30
6.89	5964249.60
12.91	5964239.60
18.95	5964232.40
24.91	5964222.90
30.92	5964214.30
36.91	5964205.70
42.90	5964198.10
48.91	5964189.50
599.30	5964091.30
1421.86	5964088.90
2244.42	5964087.00
3067.05	5964086.10
3889.61	5964086.10
86385.77	5964086.10
86936.16	5964086.10
87758.72	5964086.10
88581.28	5964086.10
89403.91	5964087.00
90226.47	5964087.50
4649.03	5964088.00
5471.60	5964088.00
6294.22	5964088.90
7116.78	5964088.90
7939.40	5964088.90
8761.96	5964088.90
9584.53	5964088.90
10407.15	5964088.90
11229.71	5964088.90
12052.28	5964088.90
14108.74	5964088.90

TABLE IX (CONTINUED)

Time (Secs)	Frequency (Hz)
14931.35	5964089.90
15754.00	5964090.80
16576.57	5964091.30
17399.19	5964091.30
18221.78	5964091.30
19044.46	5964091.80
19866.99	5964091.80
20689.66	5964093.20
21512.34	5964093.20
22334.93	5964093.20
22609.12	5964093.20

TABLE X

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL ACETATE)-TOLUENE TEMPERATURE OF FILM: 80 C TEMPERATURE OF SOLVENT BATH:50 C RUN NO: 1

Time (secs)	Frequency (Hz)
0.00	5964288.20
5.99	5964278.20
12.01	5964267.70
18.05	5964255.30
24.01	5964243.90
29.99	5964232.40
36.02	5964220.50
42.00	5964208.10
47.98	5964198.60
462.28	5964137.10
1284.85	5964135.20
2107.41	5964133.30
2930.03	5964133.70
3752.57	5964133.30
4490.40	5964133.70
5312.96	5964133.30
5450.05	5964133.30
5587.17	5964131.80
6409.79	5964133.70
7232.33	5964133.70
8054.92	5964133.70
8877.51	5964133.70
9700.10	5964133.70
10522.70	5964133.70
11345.26	5964133.70
12167.83	5964134.70
12990.42	5964134.70
13813.01	5964135.20
14772.69	5964135.60
15595.37	5964135.60
16417.91	5964136.60
17240.55	5964136.60
18063.11	5964136.60

TABLE X (CONTINUED)

Time (Secs)	Frequency (Hz)
18885.79	5964136.60
19708.35	5964136.60
20530.97	5964137.60
21353.65	5964138.00
22039.14	5964139.00

TABLE XI

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL ACETATE)-TOLUENE TEMPERATURE OF FILM: 80 C TEMPERATURE OF SOLVENT BATH:50 C RUN NO: 2

Time (secs)	Frequency (Hz)
0.00	5964303.50
6.02	5964292.50
12.06	5964279.20
18.02	5964266.30
24.03	5964252.90
30.02	5964239.60
36.04	5964227.20
42.02	5964214.30
864.59	5964142.80
1687.18	5964141.80
2509.77	5964141.80
3332.44	5964141.80
4154.98	5964141.80
4977.60	5964142.80
5800.19	5964143.80
6622.79	5964143.80
7445.34	5964144.20
8267.94	5964144.20
9090.48	5964144.70
9913.15	5964145.70
10735.69	5964146.10
11558.28	5964146.10
12380.87	5964146.10
13203.43	5964146.10
14026.05	5964146.60
14848.62	5964147.10
15671.18	5964147.10
16493.78	5964147.10
17316.39	5964147.10
18138.93	5964148.00
18961.57	5964149.00
19784.11	5964149.00
20606.71	5964149.00

TABLE XI (CONTINUED)

Time (Secs)	Frequency (Hz)
21429.35	5964149.00
22251.94	5964150.00
22526.13	5964150.00

TABLE XII

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL ACETATE)-TOLUENE TEMPERATURE OF FILM: 80 C TEMPERATURE OF SOLVENT BATH:55 C RUN NO: 1

Time (secs)	Frequency (Hz)
0.00	5964304.40
5.88	5964290.60
11.87	5964270.60
17.94	5964251.00
23.86	5964231.50
29.85	5964213.80
35.87	5964196.20
41.88	5964180.50
47.87	5964164.30
598.25	5964121.30
1009.61	5964119.90
1558.05	5964118.00
2380.58	5964116.10
3203.24	5964116.10
4025.80	5964115.60
4788.73	5964115.10
5611.29	5964115.10
6433.86	5964115.10
7256.44	5964115.10
8079.06	5964115.10
8901.60	5964115.60
9724.19	5964115.60
10546.79	5964115.60
11369.35	5964116.10
12191.97	5964115.60
13014.53	5964115.60
13837.10	5964116.10
14659.69	5964116.10
15482.31	5964116.10
16304.87	5964115.60
17127.52	5964115.60
17950.08	5964115.60
18772.73	5964115.60

TABLE XII (CONTINUED)

Time (Secs)	Frequency (Hz)
19595.32	5964116.10
20417.94	5964116.10
21240.61	5964116.10
22063.17	5964116.10
22885.74	5964116.10
23022.83	5964116.10
23708.36	5964116.10
24393.83	5964116.10

TABLE XIII

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL ACETATE)-TOLUENE TEMPERATURE OF FILM: 80 C TEMPERATURE OF SOLVENT BATH:55 C RUN NO: 2

Time (secs)	Frequency (Hz)
0.00	5964304.40
5.99	5964293.50
12.03	5964276.80
17.99	5964259.10
24.01	5964242.50
29.99	5964226.20
36.00	5964210.00
41.99	5964194.30
728.45	5964150.00
1551.07	5964146.10
2373.61	5964144.20
3196.25	5964143.80
4018.82	5964142.80
4841.49	5964142.80
5642.82	5964141.80
6465.47	5964141.80
7288.03	5964141.80
8110.63	5964141.80
8933.21	5964141.80
9755.81	5964141.80
10578.34	5964141.80
11400.96	5964141.80
12223.53	5964141.80
13046.12	5964141.80
13868.74	5964140.90
14691.27	5964140.90
15513.95	5964140.90
16336.62	5964139.50
17159.27	5964139.50
17981.83	5964139.50
18804.45	5964139.50
19627.01	5964139.00
20449.58	5964139.00

TABLE XIII (CONTINUED)

Time (Secs)	Frequency (Hz)
21272.25	5964139.00
22094.87	5964139.00
22917.41	5964139.00

Table XIV

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL ACETATE)-TOLUENE TEMPERATURE OF FILM: 80 C TEMPERATURE OF SOLVENT BATH:65 C RUN NO: 1

Time (secs)	Frequency (Hz)
0.00	5964316.40
5.99	5964295.40
12.00	5964272.00
18.02	5964249.60
24.00	5964226.20
30.02	5964203.80
35.98	5964184.80
41.99	5964165.70
48.00	5964149.00
598.38	5964129.00
1421.06	5964124.20
2191.71	5964122.30
3014.36	5964121.30
3836.90	5964119.90
4659.55	5964119.90
5482.11	5964119.90
6304.68	5964119.90
7127.24	5964119.90
7949.88	5964119.90
8772.53	5964119.90
9595.07	5964119.90
10417.72	5964119.90
11240.28	5964119.90
12062.98	5964119.90
12885.57	5964120.40
13708.16	5964119.90
14530.73	5964120.40
15353.38	5964120.40
16176.02	5964120.40
16998.58	5964121.30
17821.17	5964121.30
18643.79	5964121.30
19466.36	5964121.30

TABLE XIV (CONTINUED)

Time (Secs)	Frequency (Hz)
20288.92	5964121.30
21111.62	5964121.30
21934.22	5964121.30
22756.81	5964121.30

Table XV

TIME VERSUS FREQUENCY DATA FOR POLY(VINYL ACETATE)-TOLUENE TEMPERATURE OF FILM: 80 C TEMPERATURE OF SOLVENT BATH:65 C RUN NO: 2

Time (secs)	Frequency (Hz)
0.00	5964313.50
5.88	5964295.40
11.92	5964272.50
17.99	5964249.60
23.92	5964229.10
29.91	5964207.60
35.90	5964188.60
41.91	5964171.40
47.93	5964155.20
462.20	5964131.80
1147.78	5964127.50
1970.32	5964124.20
2792.96	5964122.30
3615.53	5964121.30
4438.15	5964121.30
5218.79	5964121.30
6863.92	5964121.30
7686.54	5964121.30
8509.21	5964121.30
9331.75	5964121.30
10154.40	5964121.30
10976.96	5964121.30
11799.61	5964121.30
12622.17	5964121.30
13444.71	5964122.30
14267.30	5964122.30
15227.04	5964122.30
15912.59	5964122.30
16735.13	5964122.30
17557.77	5964122.30
18380.34	5964122.30
19202.96	5964122.80
20025.52	5964122.80

APPENDIX B

OPERATING PROCEDURES FOR THE QUARTZ CRYSTAL MICROBALANCE

OPERATING INSTRUCTIONS FOR THE PIEZOELECTRIC QUARTZ MICROBALANCE

Preliminary Checks

1. Fill the nitrogen trap with liquid nitrogen to prevent contamination of the penetrant atmosphere in the chamber which can occur due to backstreaming of oil vapors from the rotary vane pump. The liquid nitrogen will also protect the pump from solvent vapors
2. Check the level and condition of the oil in the vacuum pump. A good indication of poor or low oil is when a vacuum of 10^{-1} to 10^{-2} torr cannot be achieved in the chamber.
3. Check the level of the water in the tank of the heating circulator. Make sure the water circulator bath is full.
4. Turn on the power supply to all the equipment.
5. Check to make sure that valves A, B, C are closed (see Figure 2) are closed.
6. Calibrate the Pirani gauge as explained in the Leybold Inficon PG3 manual.

Evacuation Procedure

The first step to run the experiment is the evacuation of the chamber which is accomplished by carrying out the following procedure. These same steps are to be followed whenever the chamber is to be evacuated:

1. Open the valve connecting the rotary vane pump to the chamber (valve A).
2. Turn on the rotary vane pump.
3. When the pressure decreases below 10^{-2} torr, close valve A.
4. Open valve B, the high vacuum gate valve.
5. Switch on the turbomolecular pump. The turbotronic display will show that the pump is in the acceleration mode. After approximately 5 minutes, when the turbomolecular pump has accelerated to its maximum speed it will switch to 'normal' mode of operation.
6. Once the turbomolecular pump has been switched on the vacuum will be reduced to below 10^{-3} torr which is the minimum that the Pirani gauge can read and hence it will display 'OFF'.
7. Switch on the hot cathode gauge, IG3, and press the 'DEGAS' switch.
8. Allow the evacuation process to proceed for approximately 3-4 hrs. This will complete the evacuation process.
9. Since the experiment has to be conducted at constant temperature, the set up has to be heated to the required temperature. This is done by switching on the blower and the heating element in the thermal box. The temperature of the box is set to the required temperature. The temperatures of the water circulator and the solvent bath are also set at the required temperatures. The temperatures are then allowed to stabilize for about 12 hours.

Diffusivity Measurements

Three steps are involved in obtaining the diffusion coefficient using the quartz crystal microbalance:

1. Measurement of the frequency of the bare crystal (see below).
2. Measurement of the frequency of the polymer coated, solvent free crystal (see below).
3. Measurement of the frequency change during the experiment.

Measuring the Frequency of the Bare Crystal

1. The bare crystal should be placed in the crystal holder and mounted in the chamber.
2. The chamber is then evacuated for about 2-3 hrs.
3. The frequency of the bare crystal should be noted in a file once it has reached a steady value.

Measuring the Frequency Of the Polymer Coated Crystal

1. Carefully remove the crystal holder from the chamber.
2. Coat the crystal with a polymer film of the required dimensions as explained in the section (Chapter III) on coating the crystal
3. Place the crystal into the holder and the holder into the chamber again.
4. The chamber should then be evacuated for 3-4 hrs.

5. The frequency of the crystal is noted once it reaches a steady value. To check if the frequency has reached a steady value, the frequency is recorded for about 15 minutes. The frequencies are recorded in a file by running the program 'XTC.BAS' on the computer that is connected to the deposition monitor. On running the program the computer asks for a file name in which to store the data. The computer then asks for the command corresponding to the type of data required. The command for obtaining the crystal frequency as the output ' S13' is entered. The computer records the frequency as a function of time.

Measuring the Change in Frequency of the Crystal as the Penetrant Diffuses into the Polymer Film

Once the frequencies of the bare and polymer coated crystal are noted, the following steps are carried out to record the change in frequency as a function of time

1. Switch off the IG3. This is because the penetrant will enter the hot cathode gauge and cause a malfunction.
2. Activate the deposition monitor by pressing the 'START' button.
3. Run the computer program and enter the file name as required.
4. Input the command 'S13'.
5. Close the gate valve B.
6. Open the penetrant inlet switch. Steps 4, 5, 6 have to be carried out as quickly as possible.
7. Switch off the turbomolecular pump.

8. After about 10 minutes switch off the rotary vane pump. Allow the experiment to run till the mass of the solvent sorbed reaches a value that remains constant for 3-4hrs.
9. The change in the frequency of the crystal is noted down as a function of time by recording the frequency of the crystal and the corresponding time in a file on the computer.

To End the Experiment

1. Close the solvent inlet valve C.
2. Turn off the computer connection.
3. Switch on the roughing pump.
4. Open Valve B, thus roughing down the chamber and evacuating it.
5. Switch off the pump after approximately 15 minutes of roughing.

APPENDIX C

LIST OF COMPONENTS USED IN THE EXPERIMENTAL SETUP

LIST OF COMPONENTS

PART NO	NAME OF THE COMPONENT	MODEL NO	MANUFACTURER
1.	Six Way Cross	C6-0600	Kurt J. Lesker Company
2.	Deposition Monitor	XTC/2	Leybold Inficon Inc.
3.	Quartz Crystal Sensor Head	750-207-G1	Leybold Inficon, Inc.
4.	Water Heating Circulator	MT	Brinkmann Inst. Inc.
5.	Roughing Pump	Trivac A 4-A	Leybold Inficon, Inc.
6.	Turbomolecular Pump	Turbovac 50	Leybold Inficon, Inc.
7.	Frequency Converter	Turbotronic NT 50	Leybold Inficon, Inc.
8.	Bellows	MHCFC03	Kurt J. Lesker Company
9.	Tee Joint	VF401	Huntington Laboratories
10.	Right Angle Valve A	EV 150	Huntington Laboratories
11	Gate Valve B	SG0400	Kurt J. Lesker Company
12	Liquid Nitrogen Trap	LNF 1000	Kurt J Lesker Company
13.	Toggle Valve C	VZCRT 'T'	Kurt J. Lesker Company
14.	Pirani Gauge	PG3	Leybold Inficon, Inc.
15.	Hot Cathode Ionization Gauge	IG3	Leybold Inficon, Inc.

PART NO	NAME OF THE COMPONENT	MODEL NO	MANUFACTURER
16.	Pirani Gauge Sensor	TR901	Leybold Inficon, Inc.
17.	Immersion Circulator	70	Fischer Scientific Co.
18.	Hot Cathode Ionization Gauge Sensor	Standard Bayard Alpert Glass Tubulated Type	Leybold Inficon, Inc.
19.	Temperature Controller for Six Way Cross	2000	LFE instruments
20.	Heating Tapes	SRT05101	Omega Technologies
21.	Heating Element	148014	Omega Technologies
22.	Temperature Controller	Omega 9000	Omega Technologies
23.	Solid State Relay	SSR240DC10	Omega Technologies
24.	Heat Sink	FHS 1	Omega Technologies
25.	Fast Blow Fuses	KAX 10	Omega Technologies
26.	Fuse Block	FB 1	Omega Technologies
27.	RTD Sensor	RTD 905	Omega Technologies
28.	Dayton Fan	40783	Granger Inc.
29.	Deposition Monitor - Computer Interface	RS232 type	

APPENDIX D

PROGRAM FOR ACQUIRING FREQUENCY DATA AS A FUNCTION OF TIME

XTC/2 RS232 COMMUNICATIONS PROGRAM WITHOUT CHECKSUM

THIS PROGRAM IS DESIGNED TO TRANSMIT INDIVIDUAL COMMANDS

```
50    OPEN "COM2:9600,N,8,1,CS,DS" FOR RANDOM AS #1
52    INPUT "ENTER FILENAME : "; N$
55    OPEN N$ FOR OUTPUT AS #2
60    NAK$ = CHR$(21): ACK$ = CHR$(6)
70    '
80    INPUT "ENTER COMMAND"; CMD$
81    FOR J = 1 TO 100
82    IF J > 60 GOTO 87 ELSE
83    FOR I = 1 TO 50000
84    NEXT I
85    GOTO 90
86    NEXT J
87    FOR K = 1 TO 1000000
88    NEXT K
90    Y1 = TIMER
92    GOSUB 130
95    Y2 = TIMER
96    Y = (Y1 + Y2) / 2!
100   LPRINT RESPONSE$, Y
105   PRINT RESPONSE$, "", Y
108   PRINT #2, RESPONSE$, "", Y
110   GOTO 86
120   '
```

TRANSMIT COMMAND AND RECEIVE RESPONSE SUBROUTINE

```
140   '
150   '–SEND COMMAND MESSAGE STREAM TO THE XTC/2—
```

```
160   PRINT #1, CMD$ + ACK$;
170 '
180 '—RECEIVE RESPONSE MESSAGE FROM THE XTC/2—
190   RESPONSE$ = ""
200   TOUT = 3: GOSUB 260
210   IF I$ = ACK$ THEN RETURN
220   IF I$ = NAK$ THEN RETURN
230   RESPONSE$ = RESPONSE$ + I$
240   GOTO 200
250   '
  READ SERIALLY EACH CHARACTER FROM THE INSTRUMENT INTO
                              VAR I$

270   ON TIMER(TOUT) GOSUB 300: TIMER ON
280   IF LOC(1) < 1 THEN 280 ELSE TIMER OFF: I$ = INPUT$(1, #1)
290   RETURN
300   TIMER OFF
310   RESPONSE$ = "RECEIVE  TIMEOUT"
320   I$ = NAK$: RETURN 290
```

APPENDIX E

PROPAGATION OF ERROR ANALYSIS ON THE DIFFUSION COEFFICIENT DATA FOR POLY(VINYL ACETATE)-WATER SYSTEM

ERROR ANALYSIS

The aim of this analysis is to find the error that has propagated into the final calculated quantity due to uncertainties in the measured quantities. The final quantity calculated is expressed as a function of the measured variables. In this type of analysis, the uncertainty associated with the measured variable is expressed in terms of its standard deviation. If we consider y as the calculated quantity, then the uncertainty in this quantity due to the measured variables x_1, x_2,....x_n is given by

$$\sigma_y^2 = \sum_{x=i}^{n}\left[\left(\partial y / \partial x_i\right)^2 \sigma_{xi}^2\right] \qquad \text{(E-1)}$$

This gives us the standard deviation or uncertainty in y due to the variables x_1, x_2,....x_n.

In this analysis, the uncertainty propagated in the diffusion coefficient due to the uncertainties in the measured variables is calculated. The diffusivity is calculated from the measured frequency of the crystal and thickness of the film.

$$D = \frac{\pi}{4} l^2 R^2 \qquad \text{(E-2)}$$

where D = diffusion coefficient

l = thickness of film

$$R = \left(\frac{\frac{d}{dt}\left(\frac{m(t)}{m(\infty)} \right)}{\sqrt{t}} \right)$$

Applying equation E-1 to equation E-2 we get

$$\sigma_D^2 = \frac{\pi}{4}\left[\left(l^2 2R\right)^2 \sigma_R^2 + \left(R^2 2l\right)^2 \sigma_l^2 \right] \qquad \text{(E-3)}$$

$$\sigma_D^2 = \pi l^2 R^2 \left[(l)^2 \sigma_R^2 + (R)^2 \sigma_l^2 \right] \qquad \text{(E-4)}$$

Here l and R are known quantities. The uncertainties in these quantities have to be estimated. The uncertainty in the thickness of the film has been estimated to be 20%. The value of R is calculated from

$$R = \left(\frac{\frac{d}{dt}\left(\frac{m(t)}{m(\infty)} \right)}{\sqrt{t}} \right) \qquad \text{(E-5)}$$

Since time t is measured and recorded by the computer clock we assume that there is no uncertainty associated with its measurement. The quantity R is simply the slope of the reduced sorption curve. The uncertainty associated with this is estimated as follows

$$\frac{M(t)}{M(\infty)}=\frac{f_{2(t)}-f_1}{f_{2(\infty)}-f_1} \qquad \text{(E-6)}$$

Here the measured quantities are the frequencies $f_{2(t)}$, $f_{2(\infty)}$, f_1. The uncertainties associated with these quantities are as follows

$f_2(t)$	0.1 Hz
f_1	10 Hz
$f_2(\infty)$	10 Hz

The uncertainty associated with $f_{2(t)}$ has been given by the manufacturer. The uncertainties associated with f_1 and $f_{2(\infty)}$ are based on experimental runs. The measured frequency of the crystal has been observed to drift by 5-6 Hz when there is no addition or depletion of mass from the crystal. 10 Hz is a very conservative estimate leading to the maximum error propagated in the diffusivity. Applying Equation (E-1) to Equation (E-6) we get

$$\sigma_R^2=a^2\sigma_{f2}^2+b^2\sigma_{f\infty}^2+c^2\sigma_{f1}^2 \qquad \text{(E-7)}$$

Here

$$a=\left(\frac{1}{(f_{2\infty}-f_1)}\right) \qquad \text{(E-8)}$$

$$b=\left(-\frac{(f_{2t}-f_1)}{(f_{2\infty}-f_1)^2}\right) \qquad \text{(E-9)}$$

$$c=\left(-\frac{(f_{2t}-f_1)-(f_{2\infty}-f_1)}{(f_{2\infty}-f_1)^2}\right) \qquad \text{(E-10)}$$

Applying these equations to each data point for an experimental run we obtain an estimate of the uncertainty associated with the quantity M(t)/M(∞). If we add these uncertainties to the original values of M(t)/M(∞), we get the maximum value of M(t)/M(∞) possible. Since there is no uncertainty associated with time, the slope obtained by plotting the new values of M(t)/M(∞) versus $\sqrt{t}$ will be the maximum slope obtained due to the uncertainties in the measurement of frequency. The difference between this slope and the original slope i.e. R, will give the uncertainty associated with the quantity R.

Once the uncertainty associated with R is known all the quantities in equation(E-4) are known and hence the uncertainty associated with the diffusion coefficient can be obtained. This uncertainty obtained will be the maximum value of the standard deviation possible since, it has been calculated using the maximum uncertainties possible in the measured quantities.

The above procedure was used and uncertainties calculated for the diffusion coefficients obtained for the poly(vinyl acetate)-toluene system. The diffusion coefficients and their respective uncertainties are tabulated in Table XVI. As can be seen the maximum error in the values of the diffusion coefficient is calculated to be about 50 %. This large value is mainly due to the extremely large uncertainty chosen for the thickness of the polymer film.

The estimated uncertainty in the thickness of the film (20%) is because some polymer solution may have been lost during the coating of the film. Therefore the thickness of the film can only vary between 80-100 % of the calculated thickness of the film. Hence the calculated value of the diffusion coefficient can be taken as the upper limit of the error bar and the lower limit would be equal to the calculated value less the calculated uncertainty

TABLE XVI

PROPAGATED ERRORS IN THE DIFFUSION COEFFICIENTS

DIFFUSION COEFFICIENTS cm^2/sec	PROPAGATED ERROR
4.06E-09 3.72E-09	1.83E-09
8.23E-09 8.32E-09	4.29E-09
1.09E-08 1.08E-08	4.94E-09
1.26E-08 1.21E-08	5.52E-09

APPENDIX F

DERIVATION OF THE EQUATION USED FOR OBTAINING THE AVERAGE DIFFUSION COEFFICIENT

DERIVATION OF THE EQUATION USED FOR OBTAINING THE AVERAGE DIFFUSION COEFFICIENT

In order to calculate the average diffusion coefficient, the amount of solvent that is sorbed by the polymer film is measured as a function of time. The sorption process of organic vapors into polymer films above their glass transition temperature can be described as Fickian diffusion. The diffusion coefficient in this case is a function of concentration.

When the experiment is conducted under isothermal conditions, without the occurrence of any chemical reactions, and if the effect of pressure on the total density of the system is negligible, the following equations describe the sorption process,

$$\rho\frac{\partial\omega}{\partial t}+\rho v\frac{\partial\omega}{\partial x}-\frac{\partial}{\partial x}\left(\rho D\frac{\partial\omega}{\partial x}\right)=0 \qquad \text{(F-1)}$$

$$\frac{\partial v}{\partial x}=-\frac{1}{\rho^2}\frac{d\rho}{d\omega}\frac{\partial}{\partial x}\left(\rho D\frac{\partial\omega}{\partial x}\right) \qquad \text{(F-2)}$$

$$\rho=\rho(\omega) \qquad \text{(F-3)}$$

$$\omega(x,0)=\omega_1 \qquad \text{(F-4)}$$

$$\omega\left[X(t),t\right]=\omega_2 \qquad \text{(F-5)}$$

$$\frac{\partial \omega}{\partial x}(0,t) = 0 \qquad \text{(F-6)}$$

$$v(0,t) = 0 \qquad \text{(F-7)}$$

$$\frac{dX}{dt} = (v)_x = x(t) + \frac{\left(\rho D \frac{\partial \omega}{\partial x}\right)_{x=X(t)}}{\left[\rho(1-\omega)\right]_{x=X(t)}} \qquad \text{(F-8)}$$

$$X(0) = L \qquad \text{(F-9)}$$

where:

ρ= Total density of the polymer-solvent mixture

ω= Mass fraction of penetrant in this mixture

v= Mass average velocity

D= Binary mutual diffusion coefficient

X(t)= position of the interface between the polymer solution and the gas phase

ω_1, ω_2= initial and boundary values for the mass fraction which are fixed by the nature of the experiment

The equations given above will reduce to the unsteady state diffusion equations for C, the concentration of the penetrant if

- The partial specific volumes can be considered constant.
- The phase volume change due to mass transfer can be neglected
- The diffusion coefficient can be assumed to be a constant

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad \text{(F-10)}$$

$$C(x,0) = C_1 \qquad \text{(F-11)}$$

$$C(L,t) = C_2 \qquad \text{(F-12)}$$

$$\left(\frac{\partial C}{\partial x}\right)(0,t) = 0 \qquad \text{(F-13)}$$

If M_t represents the total amount of substance that has diffused into the polymer film and M_∞ the corresponding quantity at time t = ∞,

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} exp\left\{ -D(2n+1)^2 \pi^2 t \Big/ 4l^2 \right\} \qquad \text{(F-14)}$$

The corresponding solution useful for small times is

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{l^2}\right)^{1/2} \left\{ \pi^{-1/2} + 2\sum_{n=1}^{\infty} (-1)^n ierfc \frac{nl}{\sqrt{(Dt)}} \right\} \qquad \text{(F-15)}$$

On simplification in the case of the early stages of the experiment for a constant D and film thickness l we get

$$D = \frac{\pi}{4} \left[\frac{d\left(M_t \big/ M_\infty\right)}{d\left(t \big/ L^2\right)} \right] \qquad \text{(F-16)}$$

Which is the equation used for calculating diffusion coefficients from the reduced sorption curve.

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Master of Science

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