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Thermophysical Properties of Penetrants in Polymers via a Piezoelectric Quartz Crystal Microbalance

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Accurate values for the equilibrium sorption and the diffusion rates of penetrants in polymers are required for many important polymer production and processing operations. This paper demonstrates the use of the quartz crystal microbalance (QCM) as a means to readily produce diffusivity and equilibrium data. The QCM exploits the well-known piezoelectric effect in quartz crystals to measure the mass sorption of a penetrant onto a polymer film. Nanogram resolution of the penetrant mass results in extreme accuracy. The mass sorbed as a function of time provides the necessary information to calculate the diffusion coefficient of the penetrant in the polymer, and the equilibrium mass provides the penetrant solubility. The flexibility and accuracy of the QCM are demonstrated by examining several sets of data. A comparison of penetrant-diffusion data obtained from two different techniques (the QCM and gravimetric sorption via a quartz spring balance) is presented to demonstrate the accuracy of the QCM. The results from an industrial coating/penetrant system are also given to demonstrate the capacity of the QCM to measure the equilibrium state.

Introduction

The study of polymer/penetrant diffusion and equilibrium has significant practical and theoretical implications. The high viscosity of polymer systems restricts mechanical means of mass transfer and makes diffusion the rate-controlling process in many important processing operations including photolithography, microelectronics, devolatilization, production and applications of electrically conducting polymers, drying of polymer coatings, and drug delivery. In modeling penetrant diffusion for industrial applications, a knowledge of the equilibrium conditions is essential in specifying the boundary conditions. From a more fundamental point of view, diffusion and equilibrium data are important in the evaluation of thermodynamic and diffusion models.

Permeation and gravimetric sorption methods are the two most commonly used techniques for determining the diffusion coefficients of polymer/penetrant systems. In a permeation experiment the amount of penetrant diffusing through a polymer film is measured as a function of time while the two surfaces of the film are exposed to different penetrant partial pressures. In a sorption experiment, a polymer that is in equilibrium with a specific penetrant vapor pressure is suddenly exposed to a different vapor pressure. The approach to the new equilibrium state is followed by weighing the polymer sample. Crank and Park (1968) pointed out several advantages of the sorption methods over the permeation methods.

The best sorption technique to date was developed by Duda and Vrentas (1968). Duda and Vrentas followed the extension of a quartz spring to measure the mass change of molten polymers in a known penetrant atmosphere. The sensitivity of the quartz spring required relatively thick polymer samples which resulted in experiments which could last for several days. Data collection was difficult to automate due to the difficulty in interfacing the quartz spring balance with a computer.

The purpose of this paper is to demonstrate that the disadvantages of previous experiments have been overcome with a newly developed quartz crystal microbalance which can measure weight changes as low as 1 ng. The apparatus can be easily interfaced to a computer, and the time required to conduct an experiment is at most 12−15 h.

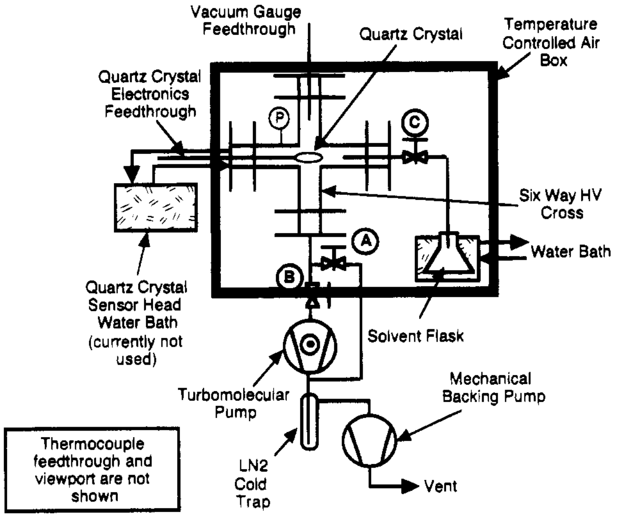

Figure 1. Schematic diagram of the quartz crystal microbalance apparatus.

Quartz Crystal Microbalance

A schematic of the quartz crystal microbalance (QCM) is shown in Figure 1. The heart of the microbalance is a thin, 0.55 in. diameter, quartz crystal coated with gold electrodes and placed in the center of an ultrahigh vacuum six-way cross. The crystal is placed in a commercially available holder and connected via electrical leads through one of the arms of the six-way cross to an excitation source and a computer-interfaced frequency monitor. The vacuum chamber is operable from 10^{-7} Torr to slight positive pressures and over a temperature range of ambient to 150 °C. A toggle valve (labeled C in Figure 1) is used to control the flow of penetrant vapors into the chamber. The jacketed flask containing the penetrant is heated with a

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circulated stream of water from a constant temperature bath. A Pirani gauge (labeled P in Figure 1) and a hot ionization gauge are connected to the chamber to measure low and high vacuum, respectively. A resistance temperature device (RTD) is placed in the chamber to measure the temperature. A rotary vane pump is used as a roughing pump, and a turbomolecular pump is used to reach high vacuum. The foreline of the rotary vane pump is connected to a liquid nitrogen trap to prevent backstreaming of vacuum pump oil into the chamber and contamination of the pump oil by solvent vapors. An insulated thermal box is used to enclose the system, and a temperature controller is used in conjunction with a heating coil and blower to maintain a constant temperature around the chamber.

Experimental Procedure

The first step in the experimental procedure is to measure the bare crystal frequency at high vacuum and at the temperature of interest. The crystal is then removed from the chamber, and a polymer film is cast onto the crystal by placing a known volume of polymer solution with a known concentration of polymer on the crystal face and allowing the solution to dry. The thickness of the deposited polymer film is calculated by assuming uniform thickness and density of the film. The coated crystal is placed in the vacuum chamber and subjected to a high vacuum to further dry the coating and eliminate contaminants. The pressure in the chamber is roughed down with the mechanical pump (valve A open, valve B closed in Figure 1) and then fully evacuated to approximately 10^{-7} Torr with the turbomolecular pump (valve A closed, valve B open).

The penetrant sorption measurement is obtained by introducing penetrant vapors into the vacuum chamber from the solvent flask. The chamber and polymer-coated crystal are heated to the desired temperature, and penetrant vapor is released into the vacuum chamber by opening the toggle valve (valve C in Figure 1). The pressure of the penetrant in the chamber is adjusted by varying the temperature of the penetrant water bath or by simply allowing penetrant to flow into the chamber for a short time and then closing the toggle valve. In either case, the penetrant pressure is measured via a digital pressure gauge attached to the chamber.

For the QCM to provide accurate measurements of thermophysical properties of penetrant−polymer mixtures, the frequency of the quartz crystal must be stable over a sufficiently wide temperature range and not exhibit temperature hysteresis. In addition, if the frequency is a known function of temperature, any temperature variations can be taken into account, which is particularly advantageous when performing measurements on a given penetrant−polymer pair over a temperature range since only a single crystal and a single bare crystal frequency measurement are required. The temperature dependence of a bare quartz crystal and a poly(vinyl acetate)-coated quartz crystal is given in Figure 2 for several temperature cycles. As is clear from Figure 2, the frequencies of both the coated and uncoated quartz crystals are stable, reproducible, and linear and exhibit no temperature hysteresis.

The frequency of the quartz crystal is measured and recorded as a function of time by a personal computer for analysis. A typical frequency response for a sorption experiment is given in Figure 3 (left axis). The QCM behaves as a harmonic oscillator, so as mass is sorbed into the polymer film through penetrant diffusion, the harmonic frequency of the crystal decreases. Experiments were performed to confirm that solvent uptake by the quartz crystal is insignificant compared to that sorbed by the polymer coating. At low mass loading the frequency change of the piezoelectric quartz crystal is proportional to the change of mass on the crystal (Lu and Czanderna, 1984):

$$m_f = \frac{-(f_c - f_q)\varrho_q \nu_q}{2 f_q^{\,2}} \tag{1}$$

where m_f is the mass of the thin film deposited on the crystal, f_c is the resonant frequency of the quartz crystal with the deposited material, f_q is the resonant frequency of the bare crystal, ν_q is the shear wave velocity, and ϱ_q is the density of quartz crystal. The time dependent behavior of f_c is used to determine the equilibrium and diffusion behavior of the polymer-penetrant system. Equilibrium is considered to be the point at which the frequency remains constant for 15−30 min.

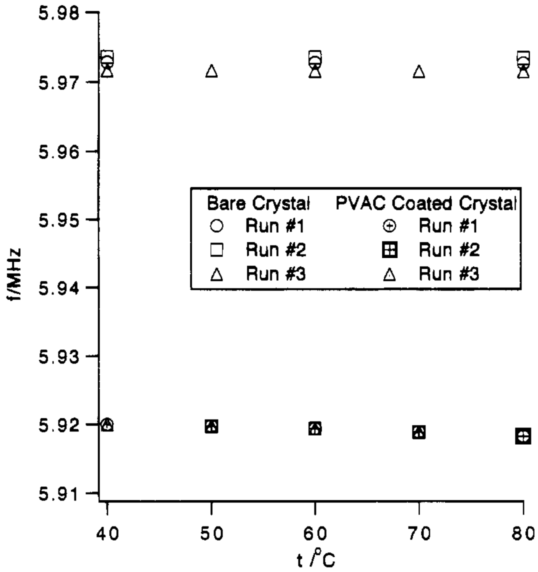

Figure 2. Temperature dependence of the frequency f of bare and coated quartz crystals.

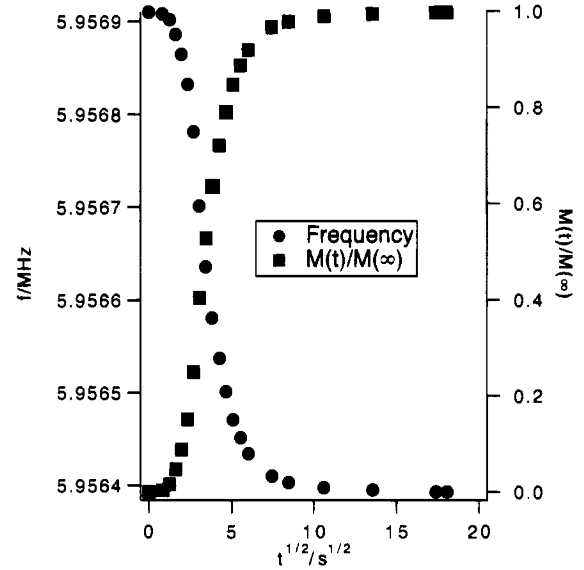

Figure 3. Frequency response and reduced sorption curve for the sorption of toluene into poly(vinyl acetate) at a film temperature of 80 °C.

The diffusion coefficient can be calculated from (Duda and Vrentas, 1971)

$$D = \frac{\pi L^2}{4}\left[\frac{\partial(M_t/M_\infty)}{\partial(t^{1/2})}\right]^2 \qquad (2)$$

where M_t represents the mass of penetrant at time t and L is the thickness of the polymer film. Equation 2 is obtained by integrating Fick's second law under the assumption of constant diffusivity. Although diffusion coefficients for most polymer–penetrant systems exhibit strong concentration dependence, all sorption techniques must make this assumption. Consequently, the assumption of a constant diffusion coefficient is a disadvantage that is not unique to the QCM, and the resultant diffusivity is actually an average value. However, the effect of the constant diffusion coefficient assumption can be minimized by making the diffusion driving force as small as possible. In practice, the error involved with this assumption can be minimized by introducing very small amounts of penetrant into the chamber for a given sorption run. Since the QCM has greater mass detection sensitivity than any other technique and smaller changes in driving force can be measured, the assumption of constant diffusivity is much less severe.

Since the frequency change of the piezoelectric quartz crystal is proportional to the change of mass on the crystal, the ratio of mass at time t to the mass at equilibrium can be found from

$$\frac{M_t}{M_\infty} = \frac{C[f_2(t) - f_1]}{C[f_2(\infty) - f_1]} = \frac{f_2(t) - f_1}{f_2(\infty) - f_1} \qquad (3)$$

where C is a proportionality constant, $f_2(t)$ is the frequency of the crystal as the penetrant diffuses into the polymer coating, and f_1 is the frequency of the polymer-coated solvent-free crystal. Equation 3 is called the "reduced sorption curve" and provides the information required to calculate the diffusivity of the polymer–penetrant system.

A typical reduced sorption curve for an experiment is also given in Figure 3 (right axis). The sorption information contained in Figure 3 allows for calculation of both the diffusivity and equilibrium mass fraction of the penetrant. The equilibrium weight fraction of the solvent sorbed by the polymer, w, can be calculated by

$$w = \frac{f_2(\infty) - f_1}{f_2(\infty) - f_0} \qquad (4)$$

where f_0 is the frequency of the bare, uncoated quartz crystal.

The activity of the penetrant can be readily determined from the pressure of the penetrant vapor in the chamber, P, and the vapor pressure of the penetrant at the temperature of the vacuum chamber, P^*, since the chamber is typically operated at low pressures (less than 101 kPa):

$$a_1 = P/P^* \qquad (5)$$

Diffusion Models for Polymer–Penetrant Systems

The free volume theory developed by Zielinski and Duda (1992) is the only known technique that is capable of predicting the polymer/solvent diffusion behavior without the use of experimental diffusion data. Zielinski and Duda (1992) derived the following expressions for calculation of the binary polymer/solvent mutual diffusion coefficients, D:

$$D = D_1(1 - \phi_1)^2(1 - 2\chi\phi_1) \qquad (6)$$

where

$$D_1 = D_0 \exp\left(\frac{-E}{RT}\right) \times \exp\left[\frac{-(w_1\bar{V}_1^* + w_2\xi\bar{V}_2^*)}{w_1\left(\frac{K_{11}}{\gamma}\right)(K_{21} - T_{g1} + T) + w_2\left(\frac{K_{12}}{\gamma}\right)(K_{22} - T_{g2} + T)}\right] \qquad (7)$$

The solvent parameters are subscripted 1 and the polymer parameters are subscripted 2 for convenience. $\bar{V}_I^*$ is the specific critical hole free volume of component 1 required for a jump, w_1 is the mass fraction of component 1, T_{g1} is the glass transition temperature of component 1, ϕ_1 is the solvent volume fraction, and χ is the polymer–solvent interaction parameter. D_0 is a constant preexponential factor, E is the energy per mole that a molecule needs to overcome attractive forces which constrain it to its neighbors, and γ is an overlap factor (between 0.5 and 1) introduced because the same free volume is available to more than one molecule. K_{11} and K_{21} are free-volume parameters for the solvent, while K_{12} and K_{22} are free-volume parameters for the polymer. The parameter ξ is the ratio of molar volumes for the solvent and polymer jumping unit volumes.

Thermodynamic Models for Polymer–Penetrant Systems

On the basis of the extensive review of Danner and High (1993), three models, Chen et al. (1990), Oishi and Prausnitz (1978), and High and Danner (1990), were selected for comparison to the experimental data.

The model of Chen et al. (1990) is a modification of the Flory equation of state so that the ideal gas limit is realized at low pressures. Another significant modification by Chen et al. over the Flory equation of state is that a group contribution approach is employed in order to make the model predictive.

The Oishi and Prausnitz model is an adaptation of the popular UNIFAC group contribution activity coefficient model (Fredenslund et al., 1977). The Oishi and Prausnitz model combines the combinatorial and residual contributions from the original UNIFAC model with an additional "free-volume" contribution specifically for polymer solutions:

$$\ln \Omega_i = \ln \Omega_i^{C} + \ln \Omega_i^{R} + \ln \Omega_i^{FV} \qquad (8)$$

The model of High and Danner (1993) is a group contribution modification of the equation of state proposed by Panayiotou and Vera (1982). This equation of state uses only the structures of the penetrant and polymer to determine the thermodynamic behavior of the mixture. The group contribution parameters were determined solely from saturated liquid densities and vapor pressures of low molecular weight compounds; no thermodynamic information from the polymer or the mixture is required for the calculations.

These three models are group contribution models and do not require thermodynamic information from the mixture as input. The Oishi and Prausnitz model does require the pure component densities, but these can be found in compilations or handbooks (e.g., High and Danner, 1993; Daubert and Danner, 1990).

Experimental Results

Two systems were studied with the quartz crystal microbalance to validate the technique. The poly(vinyl acetate)–toluene system was selected since the QCM

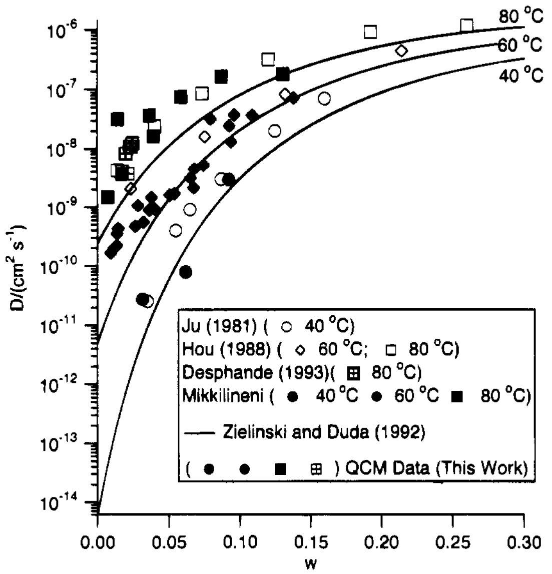

Figure 4. Mutual diffusivity *D* of toluene and poly(vinyl acetate) at various temperatures for the quartz spring balance, quartz crystal microbalance, and the free-volume theory as a function of mass fraction of toluene *w*.

results could be compared with the experimental results of other researchers, the predicted values from free-volume theory, and the predictive thermodynamic models. A second system composed primarily of a carbon black/poly(vinyl chloride-*co*-vinyl acetate) composite and methyl ethyl ketone was used as an example of the utility of the QCM to provide thermophysical information on industrially relevant systems.

For the poly(vinyl acetate)−toluene system, experiments were conducted at polymer film temperatures of 40, 60, and 80 °C. The results of these experiments, the calculated values of the diffusion coefficients from free-volume theory, and the experimental results of other researchers using a quartz spring balance are presented in Figure 4. The results from the QCM experiments are presented numerically in Table 1. As can be seen from Figure 4, the diffusion coefficients from the quartz crystal microbalance at 60 and 80 °C are in excellent agreement with those obtained by Hou (1986). The 40 °C values agree well with the free-volume theory and the quartz spring data of Ju (1981), but additional results are obviously needed to further quantify the accuracy of the QCM results at 40 °C. Experiments at 40 °C are difficult and error prone, making these data a sensitive test of the QCM technique since sorption takes place very slowly (over a period of 12 h) and the QCM frequency response is small. However, the QCM response is more significant than other gravimetric techniques. Also, the accuracy of extrapolated results from the free-volume theory at 40 °C and low concentrations is dubious.

Experimental results for the equilibrium solubility of poly(vinyl acetate)−toluene at 40 °C are given in Figure 5 along with predicted values from the models of Chen et al. (1990), Oishi and Prausnitz (1978), and High and Danner (1990). The 40 °C values agree very well with the Oishi and Prausnitz model, but are only in qualitative agreement with the quartz spring data of Ju (1981). The Oishi−Prausnitz and High−Danner models slightly underpredict the QCM measured activities of the toluene for this system. These results clearly demonstrate the extreme sensitivity of the QCM and provide additional corroboration of the technique. Experimental equilibrium sorption results for 60 and 80 °C are given in Figures 6 and 7, respectively. Again, the QCM results are in qualitative agreement with the quartz spring data (Hou, 1986) and good agreement with the Oishi−Prausnitz and High−Danner models.

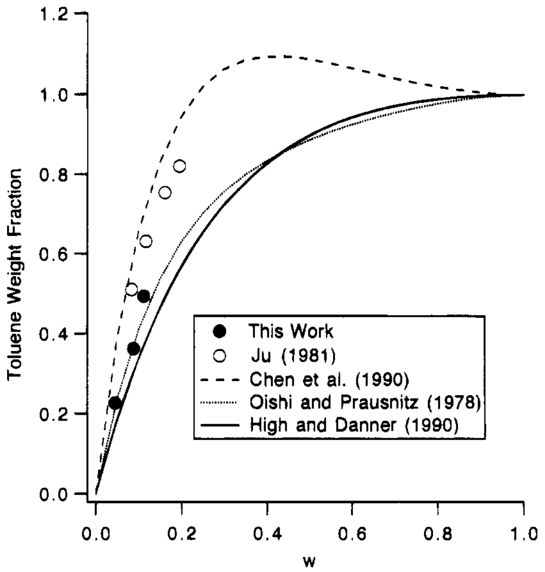

Figure 5. Equilibrium sorption of toluene and poly(vinyl acetate) at 40 °C as a function of mass fraction of toluene *w*.

Table 1. Equilibrium Sorption and Diffusivity *D* of Toluene and Poly(vinyl acetate) Measured via the Quartz Crystal Microbalance

t/°C	run no.	equilibrium solvent concn (mass %)	a_1	average solvent concn (mass %)	D/ (cm^2 s^{-1})
40	1	8.83	0.363	6.18	7.85×10^{-11}
	2	4.49	0.227	3.15	2.70×10^{-11}
	2	11.2	0.494	9.25	2.97×10^{-11}
60	1	1.30	0.096	0.91	1.64×10^{-10}
	1	3.21	0.204	2.64	4.68×10^{-10}
	1	5.87	0.316	5.08	1.62×10^{-9}
	1	7.54	0.376	6.80	4.47×10^{-9}
	1	10.53	0.485	9.63	3.72×10^{-8}
	2	1.95	0.129	1.36	2.20×10^{-10}
	2	4.90	0.264	4.02	9.22×10^{-10}
	2	8.56	0.393	7.46	5.19×10^{-9}
	2	11.87	0.484	10.88	3.68×10^{-8}
	3	1.66	0.113	1.16	2.00×10^{-10}
	3	3.88	0.224	3.21	5.49×10^{-10}
	3	6.77	0.336	6.77	2.14×10^{-9}
	3	10.54	0.448	9.41	1.30×10^{-8}
	3	15.23	0.558	13.82	7.19×10^{-8}
	4	2.06	0.112	1.44	4.29×10^{-10}
	4	4.53	0.227	3.79	1.45×10^{-9}
	5	1.97	0.114	1.38	3.49×10^{-10}
	5	4.34	0.228	3.63	8.77×10^{-10}
	5	7.48	0.342	6.54	3.16×10^{-9}
	6	4.04	0.167	2.83	1.06×10^{-9}
	6	9.35	0.369	7.95	3.17×10^{-8}
	6	7.72	0.334	5.41	1.70×10^{-9}
	7	5.43	0.054	3.80	9.94×10^{-10}
	7	10.93	0.109	9.28	2.42×10^{-8}
	7	20.40	0.204	17.56	5.63×10^{-8}
80	1	2.02	0.097	1.42	3.15×10^{-8}
	1	4.34	0.180	3.64	3.65×10^{-8}
	1	6.50	0.286	5.86	7.48×10^{-8}
	1	9.65	0.388	8.71	1.63×10^{-7}
	1	14.50	0.531	13.05	1.79×10^{-7}

In all cases, the Chen et al. (1990) model significantly overpredicts both the quartz spring data and the QCM data. In fact, the activities from the Chen et al. model exceed unity, indicating that this model predicts that the toluene−poly(vinyl acetate) system phase separates. Simple, qualitative experiments clearly show that the toluene−poly(vinyl acetate) system is miscible at all concentrations in the temperature range of 60−80 °C. Therefore, the Chen

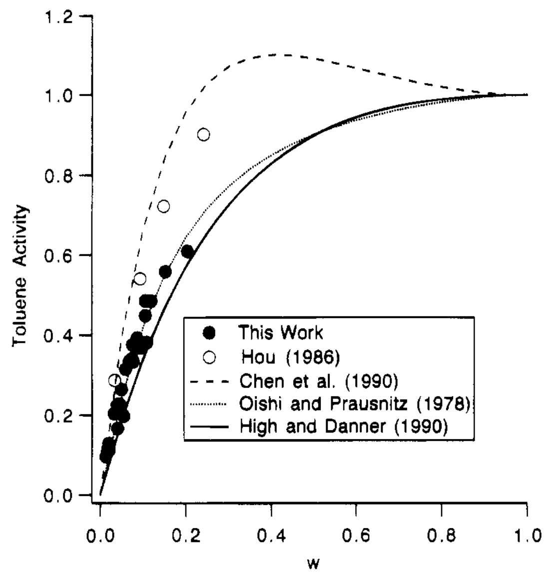

Figure 6. Equilibrium sorption of toluene and poly(vinyl acetate) at 60 °C as a function of mass fraction of toluene *w*.

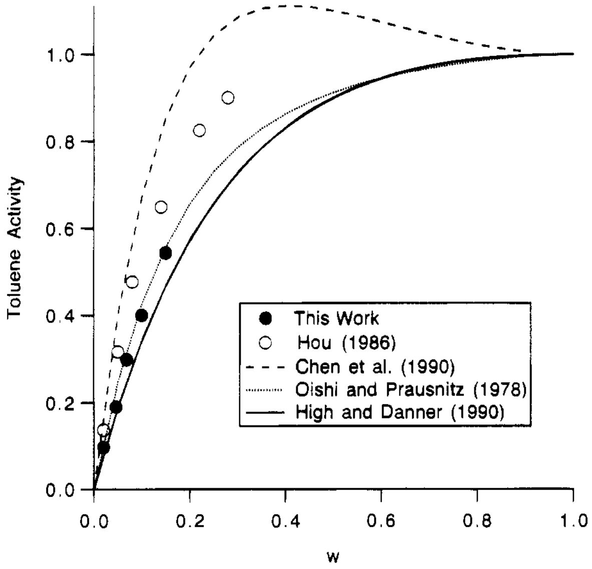

Figure 7. Equilibrium sorption of toluene and poly(vinyl acetate) at 80 °C as a function of mass fraction of toluene *w*.

et al. (1990) model does not adequately predict the toluene–poly(vinyl acetate) system.

The 40, 60, and 80 °C quartz spring data of Ju (1981) and Hou (1986) are in good agreement with the predictions from the model of Chen et al. However, as discussed above, the Chen et al. model erroneously predicts phase separation for this system and the predictions for this system by the Chen et al. model must be viewed with suspicion. As is clearly seen in Figure 6, the QCM data are very reproducible especially considering that the 60 °C QCM data were obtained from different quartz crystals coated with different film thicknesses and different experimental runs. The reproducibility of the QCM data and the excellent agreement with the Oishi and Prausnitz model leads us to believe that the QCM data are of high accuracy. An attempt is in progress to further reconcile the differences between the QCM and quartz spring data.

The ultimate goal of the QCM is to provide quantitative measurements for industrially relevant systems. To date the equilibrium sorption results from an industrially relevant system are very encouraging. Sorption runs have been performed on a random copolymer of poly(vinyl acetate) and poly(vinyl chloride) filled with carbon black and other additives. This polymer composite is an example of an industrially useful material that heretofore has not received substantial attention in the polymer science literature. The QCM results for the equilibrium sorption are provided in Figure 8, and predicted values from the Oishi and Prausnitz model for poly(vinyl acetate) and poly(vinyl chloride) homopolymers are given in Figure 8 for comparison. Interpretation of the thermodynamic behavior of filled copolymer systems is complicated, but the agreement in this case is encouraging. This example is provided not as a quantitative example of the QCM, but as a demonstration of the utility of the QCM to explore more complicated, industrially relevant systems in greater detail.

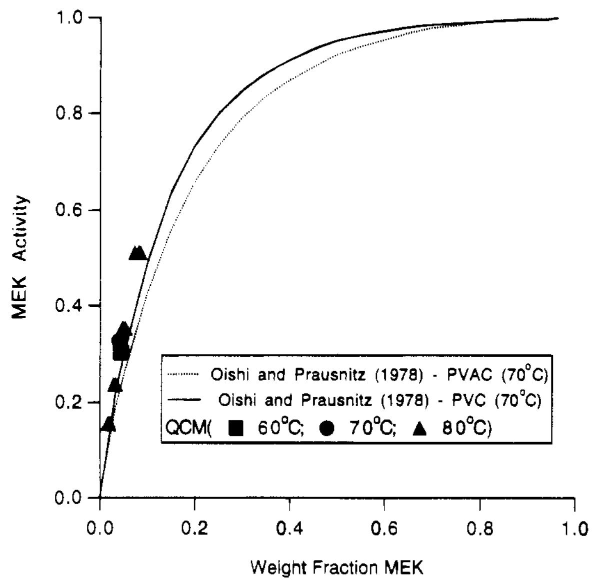

Figure 8. Equilibrium sorption of methyl ethyl ketone and carbon black filled poly(vinyl acetate-*co*-vinyl chloride) for the quartz crystal microbalance and the Oishi and Prausnitz model.

Conclusions

The QCM has proven to be a uniquely capable and extremely powerful experimental tool to measure the thermophysical properties of polymer solutions. Successful application of the technique requires extreme cleanliness in the vacuum chamber so that the quartz crystals are not susceptible to contamination. In addition, the device is particularly suitable for industrial laboratory applications since the device can easily be computer controlled.

Our results indicate excellent agreement among the QCM data, previous experimental diffusion data, and the free-volume model predictions for the poly(vinyl acetate)–toluene system. Our results also indicate favorable agreement for equilibrium sorption results between the poly(vinyl acetate)–toluene and the filled poly(vinyl acetate-*co*-vinyl chloride)–methyl ethyl ketone systems and the Oishi and Prausnitz model.

Future Work

The work presented herein represents only one example of the many potential applications of the QCM. The QCM is uniquely suited to measure the transport and thermodynamic properties of semicrystalline materials, and we are currently investigating these systems. In addition, we intend to modify our apparatus to measure the dynamic response of the polymer film to an oscillating diffusion driving force much like is done in mechanical spectroscopy for rheological measurements. Finally, we intend to investigate the use of specially coated crystals to be used as "penetrant-specific" sensors.

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