

ARTICLE

Payne cell gravimetric measurements in polymer-solvent systems for diffusion coefficients and isotherm data

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Abstract

The discussion focuses on the application of a Payne cell to the measurement of diffusion and solubility coefficients in polymer/solvent systems. Payne cells have, thus far, been used exclusively to measure steady-state permeation rates of solvents. An analytical model has been developed to describe transient gravimetric sorption and desorption measurements performed with a Payne cell. The model has been validated by a complementary numerical simulation and has been applied to evaluate diffusion and solubility coefficients in two different toluene-silicone rubber systems. The data measured using the Payne cell are found to compare very well with diffusion coefficient and isotherm data measured by traditional gravimetric sorption experiments.

KEYWORDS

coatings, membranes, theory and modeling, thermogravimetric analysis

1 | INTRODUCTION

There are several key parameters that can be used to understand the response of a polymeric material to chemical exposure. These include the permeation, diffusion, and solubility coefficients.^{1–4} The solubility coefficient (*S*) of a solvent in a polymer reflects the quantity of solvent contained with a polymer membrane at equilibrium conditions. The diffusion coefficient (*D*) defines how quickly a molecule migrates from one side of a polymer membrane to the other. The permeation coefficient (or permeability, *P*^{*}) is a combination of *D* and *S* and reflects the amount of solvent transmitted across a film or membrane in a given period of time. Consequently, if a molecule travels quickly across a membrane (*D* high) but the number of molecules transmitted is low because the solubility (*S*) of gas/vapor in the membrane is low, the overall number of molecules transmitted in a period of time (*P*^{*}) would be low. Permeation rates can, therefore, be manipulated by altering the structure/chemistry of a polymer to modify either the diffusion rate or solubility of the permeant within the membrane.

Permeation equipment is generally available to examine gas transport and water transmission, but instruments accessible to study solvent migration are relatively rare.^{5,6} Nonetheless, transmission rates of solvents and moisture through polymer films continue to be key performance indicators for various applications including packaging, encapsulation, and membrane separations. In addition, commercial units marketed to measure the transmission rates of penetrants through polymers are generally developed to examine steady state transmission rates and permeation coefficients. Quite often, however, knowledge of the diffusion rate is the critical bit of information sought after. For example, someone using nitrile gloves as a safeguard from exposure to chemicals is interested in when those chemicals begin migrating through the glove rather than the rate at which transmission occurs at steady state.

The most common traditional schemes to measure diffusion and solubility coefficients involve equipment which allows the transient sorption process to be measured either gravimetrically⁷ or via pressure change.⁸ These methods, however, are challenging to apply to

systems where the amount of uptake of the penetrant in the polymer is low or if the rate of diffusion is very slow. Another less frequently used but highly accurate experimental technique is inverse gas chromatography (IGC)⁹. For IGC the polymer is coated on a capillary column and solvent is injected into the column. The solubility and diffusivities are determined based on modeling of elution profiles. The method is generally used for the case of infinite dilution but has been expanded to the finite concentration regime.¹⁰ As with the gravimetric and pressure-decay techniques, experimental difficulties arise when the solubility and rate of diffusion of the penetrant in the polymer are low. For IGC, analysis of the elution profile under these conditions is impeded due to excessive skewing of the chromatographic peaks.¹¹

The equipment used for steady state permeation analyses may be more useful in the cases of slow diffusion and low penetrant uptake, since they involve examining the total amount of penetrant transmission through a membrane as a function of time. Although it reaches a steady state level, transmission does not stop during permeation tests, while in standard gravimetric experiments mass uptake stops when equilibrium is reached. The time dependence of the *total permeant mass transmitted through* a membrane is more easily measured than the *total permeant mass absorbed* by the membrane. To this end, application of a Payne cell is herewith considered.¹²⁻¹⁴

Payne cells are cylindrical cups in which a solid adsorbent or liquid solvent is maintained beneath a polymer film, and the opposite surface of the polymer is placed in contact with solvent vapor. In the first scenario, a vapor transmits through the polymer and is quickly scavenged by the adsorbent, thereby maintaining a constant driving force across the membrane. If a Payne cell is placed on a gravimetric balance, continuous weight uptake can be measured as a function of time. A schematic of the coupled Payne cell gravimetric sorption setup is shown in Figure 1.

In the second scenario, which is depicted in Figure 2, the Payne cell contains liquid solvent. The vapor phase

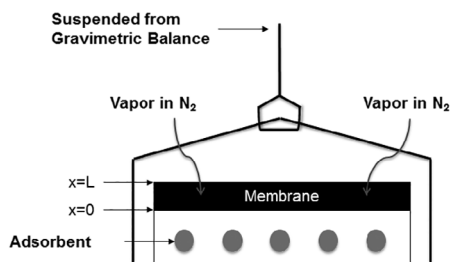


FIGURE 1 Schematic of the use of a Payne cell in a gravimetric adsorption experiment

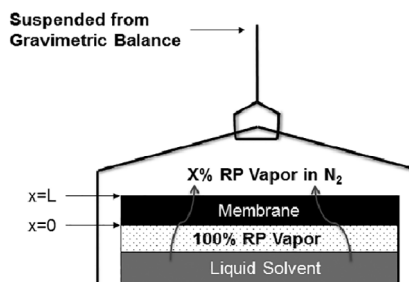


FIGURE 2 Schematic of the use of a Payne cell in a gravimetric desorption experiment

above the liquid, which is in equilibrium with the liquid phase, is maintained at 100% relative pressure (RP), or 100% relative humidity (RH) in the case of water. If the gas phase on the opposite surface of the polymer is maintained at any constant relative pressure (below 100%), the ultimate result is a net weight loss from the system as solvent desorbs from the Payne cell, through the polymer membrane into the gas phase.

In a recent work¹⁵, an analytical expression was derived to analyze a series of multi-step permeation experiments. The analysis treated diffusion through the membrane as Fickian and considered an initial concentration gradient within the polymer at the start and finish of each transient experiment. The analytical model developed enables the concentration dependence of P^* , D , and S to be evaluated easily from sequential step-change permeation experiments at conditions when no external mass transfer limitations exist. By accounting for the mass gained/lost by the membrane, along with the mass transmitted through the membrane, we have developed an analogous, yet novel, analytical model for a multistep, Payne cell experiment from which the concentration dependence of the P^* , D , and S can be evaluated. The analytical expression can be used for both the sorption and desorption experiments depicted in Figures 1 and 2. This is an advancement since, thus far, Payne cells have been employed exclusively to measure the permeation rates of solvents through polymers.¹²⁻¹⁴

The toluene/silicone rubber system is used here as a case study to evaluate the applicability of the analytical model to the measurement of diffusion coefficients and isotherm data. This system has been selected since, at ambient conditions, silicone rubber is far above its glass transition temperature and molecular diffusion is relatively fast. This condition poses a significant challenge to the adsorbent solid (see Figure 1) as to whether the rate of uptake by the solid is sufficiently fast to maintain a constant driving force across the membrane during the experiment. If the adsorbent captures solvent vapor sufficiently quickly in a fast-transmitting system

(e.g., toluene-silicone) to evaluate diffusion and isotherm data accurately, then the driving force across the membrane should be easier to maintain constant in slower transmitting systems. The Payne cell is expected to be particularly useful in these low solubility systems, which are difficult to study by traditional experiments, since it involves measuring the time dependence of the *total mass of permeant transmitted through* a membrane which is more easily measured than the *total mass of permeant absorbed* by the membrane. To validate the data measured with the Payne cell, diffusion coefficients and isotherm data have been collected by traditional techniques and used for comparison.

2 | EXPERIMENTAL

Standard diffusion and isotherm measurements were performed using a DVS Resolution dual-vapor gravimetric sorption analyzer from Surface Measurement Systems (SMS) and a Rubotherm GHP-150 gravimetric balance at 25°C. DVS measurements were flow experiments made using N₂ as a carrier gas while the Rubotherm experiments were static, that is, the system was evacuated prior to the sorption analysis, toluene vapor was introduced up to a fixed pressure and the system was held at this static condition of temperature and pressure until equilibrium was achieved.

The DVS Resolution blends a dry N₂ gas stream with a N₂ gas stream that has been saturated with solvent, in this case toluene, at different mass flow rates to achieve user-defined percent relative pressures (% RP) between approximately 5 and 95%. The solvent vapor concentration is measured directly on the unit using a speed of sound sensor. The overall flow rate of gas to the sample can be varied between approximately 50 and 200 cm³/min. Standard isotherm and diffusion measurements were performed on the unit by setting a % RP, allowing sorption to occur until equilibrium was achieved and then stepping to the next % RP point. Both absorption and desorption experiments were performed using different carrier gas flow rates to ascertain there was no film resistance at the surface boundaries. Diffusion coefficients were evaluated using a Fickian sorption analysis with slab geometry. Since the DVS Resolution is a flow through unit, the overall pressure around the sample was maintained at approximately 1 atm, even when the % RP was changed. Consequently, no buoyancy correction to the experimental data was needed.

The Payne cell experiments discussed in the work were also measured on a DVS Resolution system and will be discussed in more detail within the manuscript. The Payne cell used had an active sample diameter of 6.5 mm

and contained approximately 200 mg of Norit activated carbon. The total pore volume and BET surface area of the adsorbent were 0.52 cm³/g and 1013 m²/g and sorbed approximately three times the amount of toluene as the silicone rubber at saturation conditions. The two silicone rubber samples examined in this study were obtained from McMaster-Carr. The materials were both approximately 0.15 cm thick and differed only in their durometer rating. Optical microscopy and Fourier transform infrared (FTIR) analysis confirmed that the materials were dense rubber samples comprised solely of poly(dimethyl siloxane).

Several complementary experiments were performed on a Rubotherm GHP-150 gravimetric balance. The Rubotherm is a high-pressure gravimetric sorption instrument capable of measuring adsorption and desorption isotherms with solid samples using a variety of gases or vapors. The balance has a 25 g capacity with a resolution of 10 μg. For the most common experimental temperatures, control to within ±0.2°C is achievable. For the gravimetric experiments conducted here, the maximum pressure attained was only 25 mm Hg (90% RP), since the saturation vapor pressure for toluene at 25°C is 27.86 mm Hg. A helium buoyancy experiment was performed over a comparable gas density range as used in the toluene experiment. Due to the low-pressure conditions under which the toluene sorption experiments were performed, no buoyancy correction to the experimental data was needed, particularly that the amount of toluene sorption measured was high.

Lastly, several weight-loss transmission tests were performed for comparison based on the traditional wet cup method.^{13–14} Permeation cups for this type of testing are available from Thwing-Albert and this weight loss experiment can be viewed as a macroscopic Payne cell experiment. Here, a permeation cup was first filled with toluene and then a pre-dried, silicone rubber membrane was sealed over the solvent. The area available for solvent transmission was either 3.9 or 14.2 cm², since two different cups were available. The air gap between the membrane and the surface of the liquid was minimized to suppress any gas-phase resistance to mass transfer. The initial weight of the cell was recorded on a 4-place AE-240 Mettler balance and weight loss measurements were conducted as a function of time. The permeation cup was maintained in a laboratory hood at 25°C between measurements.

3 | THEORY

Small concentration steps are typically made in gravimetric or manometric experiments to minimize the effect of

concentration on the transport coefficients during the step. The concentration dependence of D is evaluated by performing a series of incremental, concentration steps. Payne cell sorption experiments are also conducted in this manner. Consequently, the basic equation that describes transport through the polymer membrane during a Payne cell experiment is Fick's second law with a constant diffusion coefficient,¹ namely:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

For this analysis, a linear concentration profile is assumed to extend across the membrane from C_{2p} at $x = L$ to C_{1p} at $x = 0$ at the start of the test. Although linear, the initial profile can either be flat ($C_{2p} = C_{1p}$) or can indicate a steady-state sorption profile which resulted from the end of the previous step experiment. The initial concentration profile of solvent within the membrane is written as:

$$C_o(x) = C_{1p} - [C_{1p} - C_{2p}] \frac{x}{L} \quad (2)$$

Equation 2 will always be valid for an initial experiment where the membrane contains no solvent. A linear concentration profile is also the natural result of a one-dimensional diffusion process in which the diffusion coefficient is constant for the course of the experiment¹; consequently, Equation 2 is expected to be valid for subsequent experimental steps in systems which exhibit little or no diffusion coefficient concentration dependence. Idealized initial and long-term (steady-state) concentration profiles for the scenarios depicted in Figures 1 and 2 are shown in Figure 3.

The gas phase composition (C_g) below the membrane at $x = 0$ is assumed to be constant during the Payne cell experiment. In the case of an adsorption experiment, as depicted in Figure 1, in which the Payne cell contains a high surface area adsorbent solid, $C_g \approx 0$. In order to maintain this condition, uptake by the adsorbent must be fast compared to transmission through the membrane so that the surface concentration at $x = 0$ is held constant, that is, $C_1 = 0 \text{ g/cm}^3$. This is a critical assumption in the analysis and has been checked in the current study by performing traditional DVS sorption measurements on a silicone rubber membrane, the activated carbon adsorbent, and with an empty pan. A comparison of the rate of weight gain is provided in Figure 4 for an experiment in which the relative pressure of toluene around the sample was stepped from 0 to 30% RP at 25°C.

As is shown in Figure 4, for the tests performed in this study, the rate of toluene adsorption onto the

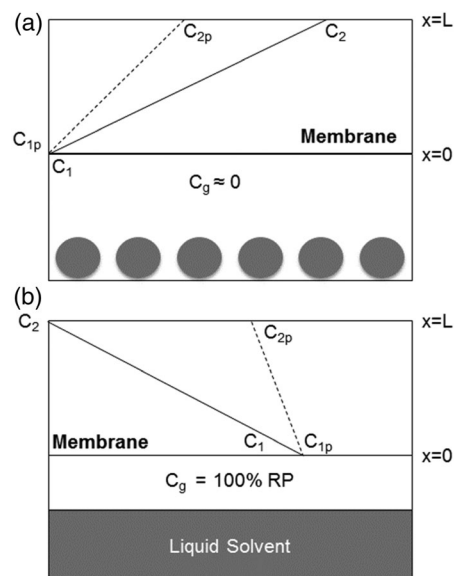


FIGURE 3 Schematic of idealized, initial and steady-state, concentration profiles assumed for development of the general analytical expression to described weight changes in a Payne cell experiment. C_1 , C_2 , C_{1p} , and C_{2p} are solvent concentrations within the membrane. Subscript “p” indicates the initial condition of the experiment based on the previous step. C_g represents the gas phase vapor concentration, which is presumed to be equal to 0 when an adsorbent is present (see Figure 3(a)) and corresponds to 100% RP for the desorption experiment depicted in Figure 3(b). C_2 represents the vapor concentration within the membrane at $x = L$, that is, the membrane surface which is exposed to external conditions

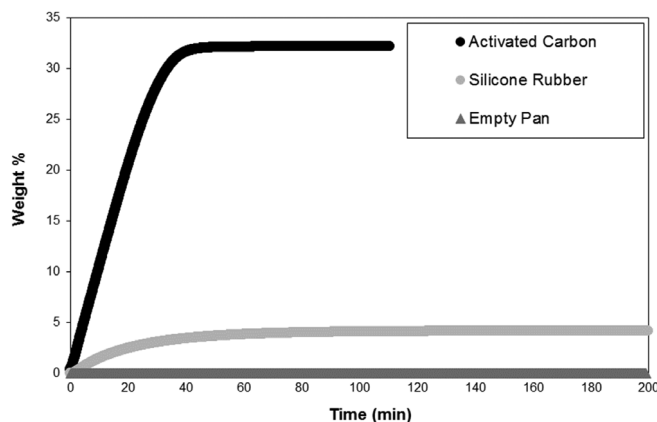


FIGURE 4 Comparison of the percentage weight change as a function of time for silicone rubber (Sample 1) and activated carbon during a traditional DVS sorption experiment performed at 25°C and for a step change of toluene relative pressure from 0% to 30%. The activated carbon, which is used in an adsorption Payne cell experiment, is seen to have much greater and faster weight uptake than the silicone rubber. Also shown is an experiment with an empty pan, confirming that no toluene sorption is observed

adsorbent was appreciably faster than the transmission rate through the silicone rubber membrane and the adsorbent has a high toluene sorption capacity. If the adsorbent captures solvent vapor sufficiently quickly, in this fast-transmitting system to evaluate diffusion and isotherm data accurately, then the driving force across the membrane should be easier to maintain constant in slower transmitting systems. The effective diffusion rate for solvent uptake onto the adsorbents in these systems will likely be faster due to less slowdown from adsorption.^{16,17} Adsorbents should be judiciously selected for Payne cell experiments in order to maintain high capacity and a low solvent concentration in the vapor phase above the solid, e.g., a zeolite for water studies, activated carbon for organic solvents, etc.

For the desorption experiment depicted in Figure 2, the membrane facing the liquid will be presumed to be in equilibrium with the gas phase at $x = 0$ which is at 100% relative pressure. C_g , therefore, is the gas phase solvent concentration that corresponds to 100% RP. For an ideal gas, C_g (g/cm^3) can be calculated from the ideal gas law ($=PM/RT$), where P and M are the vapor pressure and molecular weight of the solvent. Since the gas phase concentration is held constant, the concentration of solvent within the membrane at $x = 0$, that is, C_1 , is also maintained constant throughout the experiment. The gas phase composition at the exterior surface of the membrane ($x = L$) is also assumed to be constant throughout the experiment; however, the gas phase at this external surface can either be maintained at a concentration of $0 \text{ g}/\text{cm}^3$, as in the case of exposure to a dry sweep gas, or at a finite concentration if a partially hydrated/solvated gas stream is used.

Equation 1, therefore, is subject to the initial condition described by Equation 2 and boundary conditions

$$\text{Boundary Condition 2 } (t > 0, x = 0) : C(0, t) = C_1 \quad (4)$$

Here, C_1 is the permeant concentration within the membrane on the $x = 0$ side of the polymer while C_2 is the corresponding concentration on the $x = L$ side. It should be recognized that although the initial and steady-state concentration profiles through the membrane (depicted in Figure 3) are linear, the unsteady-state concentration profile from the beginning of the sorption process to steady state will evolve over time and will not be linear.

Although there may be concern regarding the swelling of a polymer during sorption leading to a nonlinear steady-state, concentration profile, Crank has shown that it is not the nonlinear isotherm that is of consequence, but rather concentration-dependent diffusion coefficients which give rise to non-linear concentration profiles. There have been numerous investigations examining the transient mass transfer process and the development of the concentration profile within the sample^{18–20} revealing that our assumption of a linear concentration profile is valid when the diffusion coefficient is approximately constant. In addition, the concentration profiles of permeating solvents in polymer membranes have been measured by in situ confocal Raman spectroscopy with “depth scans” through the membrane to validate the multicomponent transport in the membrane.^{21,22}

The time-dependent concentration profile, $C(x, t)$, described by Equations 1–4 has been previously derived.¹⁵ The expression for the mass per unit area gained by the membrane can be developed by integrating the concentration profile within the membrane from $x = 0$ to $x = L$ at any time, t . Based on the $C(x, t)$ profile, the resulting expression for mass per unit area within the membrane as a function of time is derived here to be:

$$M_t = \frac{[C_2 + C_1]L}{2} + \frac{2L}{\pi^2} \sum_{n=1}^{\infty} \left[\frac{C_2(-1)^n - C_1}{n^2} \right] \left[\exp \left[\frac{-Dn^2\pi^2 t}{L^2} \right] \right] \left[\frac{1 - (-1)^n}{n} \right] + \frac{2L}{\pi^2} \sum_{n=1}^{\infty} \left[\frac{C_{1p} - C_{2p}(-1)^n}{n^2} \right] \left[\exp \left[\frac{-Dn^2\pi^2 t}{L^2} \right] \right] \left[\frac{1 - (-1)^n}{n} \right] \quad (5)$$

that reflect constant surface concentrations at both sides of the membrane, namely:

$$\text{Boundary Condition 1 } (t > 0, x = L) : C(L, t) = C_2 \quad (3)$$

In the scenarios described in Figures 1 and 2, C_2 can either be greater or less than C_1 . In either case, the system will eventually reach a steady state, but there will be a continuous flux through the face of the polymer

membrane at $x = L$. In terms of the Payne cell experiment, this flux causes either an on-going weight increase to the system in the case of an adsorption experiment (Figure 1) or a continuous weight decrease for a desorption experiment (Figure 2).

The total mass of permeant transmitted through the membrane area in a given period of time at $x = L$ ($Q_{t,x=L}$) can be determined by summing the flux at the polymer-gas phase interface ($x = L$) over time:

$$Q_{t,x=L} = \int_0^t D \left(\frac{\partial C}{\partial x} \right)_{x=L} dt \quad (6)$$

The observable weight change on the gravimetric sorption balance per membrane area during a Payne cell experiment, based on constant permeant concentrations at both membrane surfaces and with a linear permeant concentration distribution, as described by Equation 2, initially present with the polymer is derived here to be:

$$Q_{t,x=L} = \frac{D[C_2 - C_1]t}{L} + \frac{2L}{\pi^2} \sum_{n=1}^{\infty} \left[\frac{C_2 - C_1(-1)^n}{n^2} \right] \left[1 - \exp \left[\frac{-Dn^2\pi^2 t}{L^2} \right] \right] + \frac{2L}{\pi^2} \sum_{n=1}^{\infty} \left[\frac{C_{1p}(-1)^n - C_{2p}}{n^2} \right] \left[1 - \exp \left[\frac{-Dn^2\pi^2 t}{L^2} \right] \right] \quad (7)$$

Here, $Q_{t,x=L}$ represents the weight per membrane cross-sectional area that is added to the system during an adsorption experiment or the solvent weight per area lost during a desorption experiment.

The steady state observable weight change per unit area on the gravimetric sorption balance can be evaluated by considering the behavior of Equation 7 at long times. The resulting expression for the total mass of permeant passing through the polymer area at $x = L$ at steady state ($Q_{t\infty,x=L}$), when a linear concentration gradient initially exists within the membrane, is:

$$Q_{t\infty,x=L} = \frac{D[C_2 - C_1]t}{L} + L \left[\frac{(C_1 - C_{1p})}{6} + \frac{(C_2 - C_{2p})}{3} \right] \quad (8)$$

In a standard permeation experiment, there is a time lag before a gas sensor registers a change in gas phase concentration below $x = 0$, since there is a finite time associated with diffusion across the membrane. In contrast, for the Payne cell adsorption experiment, weight change is observed immediately by the gravimetric balance when the external surface of the membrane ($x = L$)

is exposed to a finite solvent concentration. Consequently, extrapolation of the long-term behavior of Equation 8 to the time axis does not yield the same time-lag expression as for a typical permeation experiment.

At steady state, the rate of weight change of the gravimetric reading is equal to the transmission rate through the membrane, which, in the case of water, is reported as the moisture or water vapor transmission rate (MVTR or WVTR). One should recognize, however, that transmission rate is simply another expression for solvent flux through the membrane. By examining the transient behavior of the sorption process, therefore, one can obtain information regarding the diffusion and equilibrium characteristics of the solvent-polymer system rather than exclusively the steady state transmission rate and permeation data.

In general, for a Payne cell adsorption experiment C_1 , C_{1p} , and C_{2p} are known quantities. Consequently, the diffusion coefficient, D , and the surface concentration, C_2 , can be evaluated using a linear fit of Equation 8 to the

steady-state region of the mass uptake experiment. Alternatively, D and C_2 can be evaluated by a least-squares regression analysis of the entire sorption curve using Equation 7. On the other hand, for a Payne cell desorption experiment, in which the concentration steps at $x = L$ are taken from high levels to low, there are generally three unknown quantities: D , C_1 , and C_2 for each step experiment, rendering a linear analysis impossible and forcing one to apply a three-parameter non-linear regression analysis to evaluate the unknowns. Only in the final desorption step, when C_2 is experimentally maintained at 0 g/cm^3 , are there only two unknown parameters that can be evaluated by a linear analysis. By performing the analysis on the final desorption step first, one can eliminate an unknown variable from the prior step, thereby enabling a linear analysis for two unknowns for the previous steps.

The analytical solutions presented here have been validated by a complementary numerical simulation which, expectedly, yields identical results to the analytical model. Performing this comparison provides a validation of the numerical results and a sound platform from which to examine more complicated systems,

e.g., concentration-dependent and multicomponent diffusion processes, for which development of analytical expressions is significantly more challenging or is simply not possible.

4 | RESULTS AND DISCUSSION

Gravimetric sorption techniques have been widely used to measure solvent isotherms and to extract diffusion coefficients from transient sorption experiments.^{1,7} To minimize experimental errors, small concentration steps are generally taken and the change in sample thickness is accounted for from step-to-step. In addition, analyses have been performed which show how best to associate a diffusion coefficient to the average concentration within the interval over which it is measured.⁷

Most homopolymers of practical importance are compositionally uniform, at least on non-microscopic levels, and diffusion coefficients represent an average rate of transport over the space. Vrentas and Duda⁷ showed that for a step-change transient sorption experiment with these materials, if the diffusion coefficient is seen to increase with concentration, then the diffusion coefficient is best associated with the concentration at 70% of the interval. For example, if a polymer is initially dry, the weight percent loading of solvent within the membrane is 0. Consider a sorption experiment in which the polymer is exposed to 30% RP and the equilibrium loading of solvent within the polymer at the conclusion of the experiment reaches 3 wt%. The equilibrium point on an isotherm would be placed at a loading of 3% and at 30%

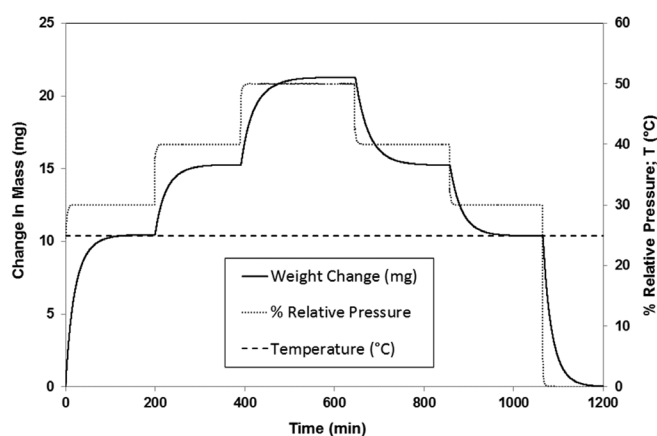


FIGURE 5 Three step traditional gravimetric sorption-desorption experiment performed with toluene and silicone rubber (Sample 1) at 25°C using a DVS Resolution dual-vapor gravimetric sorption analyzer from Surface Measurement Systems (SMS). Data can be plotted to provide isotherm data or analyzed to provide diffusion coefficient data as a function of concentration

RP. The diffusion coefficient evaluated from the transient response curve, however, would be associated with a concentration of 2.1 wt% ($= 0 \text{ wt\%} + 0.7 \times [3 \text{ wt\%} - 0 \text{ wt\%}]$). When the diffusion coefficient decreases with concentration, Vrentas and Duda evaluated that the diffusion coefficient was best associated with 56% of the concentration step.

If concentration steps are small, not much error is generally introduced with evaluating the average concentration for a diffusion coefficient. As will be seen in the upcoming data analyses, however, for large step changes substantial error can be introduced when associating a diffusion coefficient to an average solvent concentration. The Vrentas-Duda concentration assignment has been applied to the diffusion coefficients evaluated in this work as it has for numerous studies over the years. These studies indicate self-consistency between diffusion coefficients measured by different techniques including: gravimetric sorption, pressure-decay, inverse gas chromatography, dynamic light scattering and Forced Rayleigh Scattering,^{23–26} and that the polymer space probed by these diffusion experiments can be considered uniform.

A typical, traditional gravimetric sorption-desorption experiment is shown in Figure 5 for the system of toluene and silicone rubber at 25°C. Sorption steps of 0–30–40–50% RP were taken as were three desorption steps from 50–40–30–0% RP, thereby yielding six diffusion coefficients and five isotherm points (if one discounts the origin). A polymer film was suspended in a

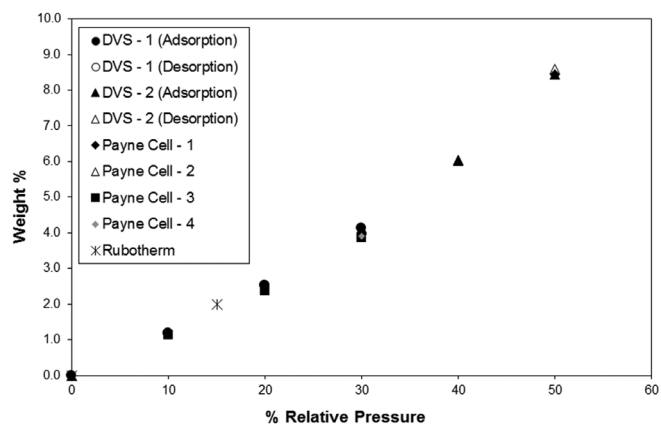


FIGURE 6 Isotherm data for toluene and silicone rubber (Sample 1) measured at 25°C. Data were measured by traditional gravimetric sorption analyses (DVS and Rubotherm) and by Payne cell experiments. Both the DVS and Payne cell experiments were conducted with a resolution dual-vapor gravimetric sorption analyzer from Surface Measurement Systems (SMS) using N₂ as a carrier gas. In comparison, the isotherm point measured on the Rubotherm balance was run in static mode

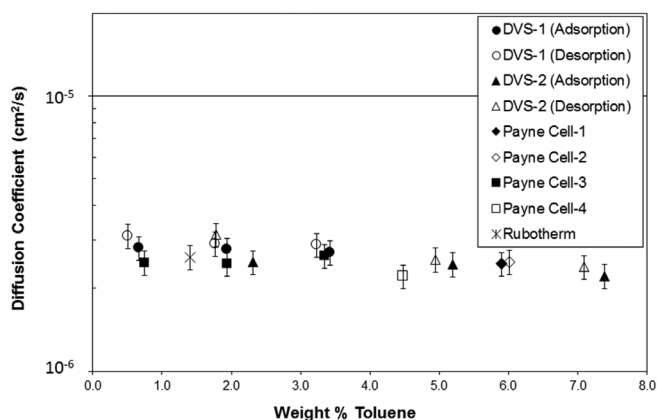


FIGURE 7 Diffusion coefficient data for toluene and silicone rubber (Sample 1) measured at 25°C. Data were measured by traditional gravimetric sorption analyses (DVS and Rubotherm) and by Payne cell experiments. Both the DVS and Payne cell experiments were conducted with a Resolution dual-vapor gravimetric sorption analyzer from Surface Measurement Systems (SMS) using N₂ as a carrier gas. In comparison, the isotherm point measured on the Rubotherm balance was run in static mode

DVS Resolution dual-vapor gravimetric sorption analyzer from SMS for these measurements.

The isotherm data from the experiment shown in Figure 5 and from other subsequent experiments are plotted in Figure 6 and show equilibrium weight percent of toluene within the silicone rubber as a function of the % relative pressure. Both the adsorption and desorption data are in good agreement showing no signs of

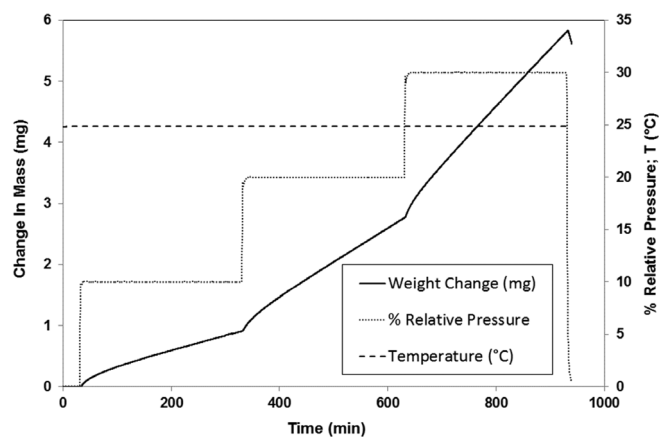


FIGURE 8 Three step, Payne cell adsorption experiment performed with toluene and silicone rubber (Sample 1) at 25°C using a DVS resolution dual-vapor gravimetric sorption analyzer from surface measurement systems (SMS). The data illustrate that diffusion can be observed during the transient measurement and that steady-state transmission can be seen in the long-term behavior

hysteresis as one would expect for a non-porous, rubbery polymer system.

A one-dimensional Fickian diffusion analysis using slab geometry¹ was performed on the transient sorption data (Figure 5) to evaluate the diffusion coefficients. These data are provided in Figure 7 and reveal diffusion coefficients that decrease slightly with increasing solvent concentration; consequently, (as discussed above) the diffusion coefficient was associated with the concentration at 56% of the concentration interval.⁷ This concentration dependence is expected in polymer-solvent systems that are far above the system glass transition temperature.^{25,26} The error associated with the evaluation of diffusion coefficients by traditional techniques is on the order of 15% and are therefore represented with error bars in Figure 7. The traditional DVS experiments were performed using different carrier gas flow rates to ensure there were no issues associated with a boundary layer resistance. In addition, a separate Rubotherm experiment was performed, in which the system was first evacuated, and solvent vapor was subsequently introduced and held at a fixed pressure of 4.18 mm Hg (RP = 15%) at 25°C. The Rubotherm experimental methodology eliminates the possibility of a boundary layer due to a carrier gas, since no carrier gas is used in the static experiment. The isotherm point and diffusion coefficient evaluated in the Rubotherm experiment is found to be in excellent agreement with the DVS results.

A series of comparable transient Payne cell permeation experiments were performed to examine whether diffusion and isotherm data could be evaluated in addition to the steady-state transmission rate. A three-step Payne cell experiment performed with toluene and silicone rubber (Sample 1) at 25°C is shown in Figure 8. The data were measured using a DVS Resolution dual-vapor gravimetric sorption analyzer from Surface Measurement Systems (SMS) and illustrate the initial weight gain due to sorption in the polymer and a long-term, steady state, weight gain that is associated with transmission through the membrane and uptake by the adsorbent contained within the Payne cell.

The three-step experiment shown in Figure 8 as well as several single step experiments were analyzed using Equation 8 to evaluate D and C_2 (since C_1 and C_{1p} were maintained equal to zero) at each step condition. Since the mass uptake is commonly measured in units of grams and the membrane area and thickness are reported in units of cm, the equilibrium solvent concentration from analysis of the weight uptake data using Equation 8 is in units of g/cm³ solution. Here, cm³ solution refers to the volume of the solvent-swollen polymer. In these units, the solvent concentration is referred to as the mass concentration²⁷ and is generally denoted as ρ_1 , while the

polymer concentration is denoted as ρ_2 . Using this nomenclature, one should recognize that $C_1 = \rho_1(x = 0)$ and that $C_2 = \rho_1(x = L)$.

In a traditional sorption experiment, an equilibrium point is formed instantly at the surface of the polymer and once equilibrium is reached every position in the polymer has the same solvent concentration as the surface point. During a Payne cell experiment, however, the solvent mass concentration (ρ_1) varies across the membrane, $C(x,t)$. The only locations where equilibrium (isotherm) points can be evaluated during a transient experiment is at the surfaces of the membrane where % RP is experimentally set.

Comparison of the isotherm data (C_2 vs. % RP) measured in the Payne cell experiment to the isotherm data measured gravimetrically (wt% solvent vs. % RP) requires some understanding of the properties of the mass concentrations and a mixing rule which indicates how much a polymer swells upon exposure to solvent. The mass density of the polymer solution (ρ) is related to the solvent (ρ_1) and polymer (ρ_2) mass concentrations through:

$$\rho = \rho_1 + \rho_2 \quad (9)$$

Furthermore, the mass fraction of solvent (W_1) and polymer (W_2) within the polymer membrane can be expressed as:

$$W_1 = \frac{\rho_1}{\rho}; W_2 = \frac{\rho_2}{\rho} \quad (10)$$

If one assumes ideal mixing based on the mass density of the pure solvent, ρ_1^* , and the pure polymer, ρ_2^* , one can define a relationship for the mass density of the polymer solution to be:

$$\frac{1}{\rho} = \frac{W_1}{\rho_1^*} + \frac{W_2}{\rho_2^*} \quad (11)$$

By combining Equations 9 through Equation 11, one can develop an expression for the mass concentration of polymer, namely:

$$\rho_2 = \rho_2^* \left[1 - \frac{\rho_1}{\rho_1^*} \right] \quad (12)$$

As a reminder, ρ_1 at $x = L$ is identical to the concentration (C_2) evaluated in the Payne cell experiment from application of Equation 8. For the toluene/silicone rubber system under consideration, the pure component mass densities of toluene and silicone rubber are 0.862 and 1.545 g/cm³, respectively. Consequently, ρ_2 can be evaluated from Equation 12. The mass density of the polymer

solution, ρ , can then be evaluated from Equation 9, and then the solvent and polymer weight fractions from Equation 10. The weight percentage of solvent within the membrane at equilibrium (as shown in Figure 6) represents grams of solvent per gram of polymer. This is nothing more than the ratio of the weight fractions ($W_1/W_2 \times 100$).

Using the relations shown in Equations 9–12, finally allows for a comparison of the isotherm data measured from the Payne cell permeation experiment to the data measured using the traditional gravimetric sorption approach. This comparison is made in Figure 6 and reveals excellent agreement in the isotherm data measured by the three experimental systems (DVS, Rubotherm and Payne cell). Likewise, a comparison of the diffusion data measured by the Payne cell permeation test versus those from a Fickian analysis of the traditional, transient sorption data is shown in Figure 7. Again, excellent agreement is found in the diffusion coefficient data measured by the three different experimental techniques. The linear initial concentration profile assumption, Equation 2, is found to be a valid assumption for analyzing the Payne cell data, since the data are collected until steady state is reached and there is little concentration dependence for the diffusion coefficients in the toluene-silicone rubber system at the temperature of the experiments performed.

For the final data comparison, standard gravimetric data measured on a Rubotherm sorption balance are compared with data measured by a permeation cup weight loss method^{13,14} which, effectively, is a pseudo-Payne cell experiment. The toluene-silicone rubber system was examined again, with a silicone specimen

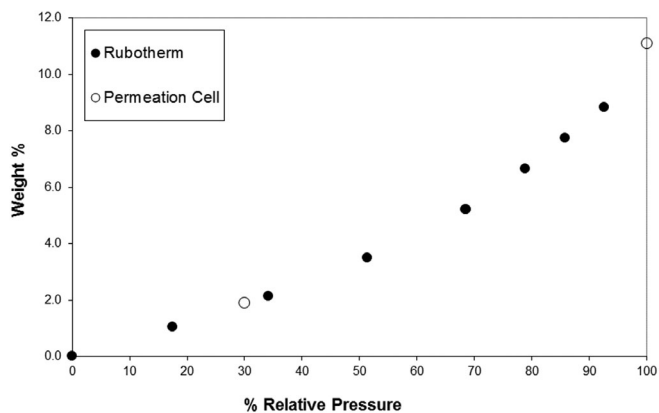


FIGURE 9 Isotherm data for toluene and silicone rubber (Sample 2) measured at 25°C. The gravimetric data were measured in the traditional manner using a Rubotherm sorption balance. The two permeation cell isotherm points were by a permeation cup weight-loss method which, in effect, is a pseudo-Payne cell desorption, permeation experiment

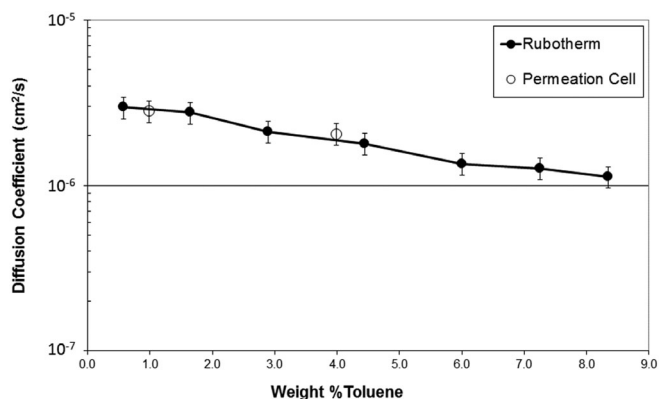


FIGURE 10 Comparison of diffusion coefficient data for toluene and silicone rubber (Sample 2) measured at 25°C. The gravimetric data were measured in the traditional manner using a Rubotherm sorption balance. The two, permeation cell diffusion coefficient points were measured by a permeation cup weight-loss method which, in effect, is a pseudo-Payne cell desorption, permeation experiment

(Sample 2) of similar thickness to Sample 1 but of greater durometer. The % RP sorption steps performed were: 0–18–34–51–69–79–86–93% RP. The isotherm and diffusion coefficient points evaluated from Rubotherm data are provided in Figures 9 and 10, respectively.

A schematic of the permeation cup set-up is depicted in Figure 11 alongside a typical set of weight loss data. For the initial test, the cup was first filled with toluene and then a silicone rubber membrane was sealed over the solvent. The air gap between the membrane and the surface of the liquid was minimized to suppress any gas-

phase resistance to mass transfer. The concentration of solvent within the membrane at the polymer/solvent vapor interface ($x = 0$) was maintained at a constant value throughout the experiment due to exposure to saturated solvent vapor. The surface of the membrane exposed to ambient conditions ($x = L$) was maintained at a toluene relative pressure of zero, since any toluene that transmitted through the membrane was swept away by the flow of gas within the hood.

Under these conditions, there is no solvent initially in the membrane ($C_{1p} = C_{2p} = 0$) and the exterior surface of the membrane at $x = L$ also contains no solvent ($C_2 = 0$). The general equation for the Payne cell experiment (Equation 8) can, therefore, be simplified to:

$$Q_{t\infty, x=L} = -\frac{DC_1 t}{L} + \frac{C_1 L}{6} \quad (13)$$

Extrapolation of the long-time weight loss behavior of the data to the y-axis ($t = 0$) enables evaluation of the solvent concentration (C_1) in the membrane at 100% RP, which is also the mass concentration of solvent, ρ_1 , in Equations 9–12. The diffusion coefficient can then be calculated from the slope of the line. The isotherm point at 100% RP from the desorption experiment was transformed to weight percentage loading using Equations 9–12 and is compared to the isotherm data measured by traditional means in Figure 10. The data from the two methods are in good agreement; however, the point measured from the desorption experiment is at higher % RP than is achievable by regular gravimetric sorption experiments.

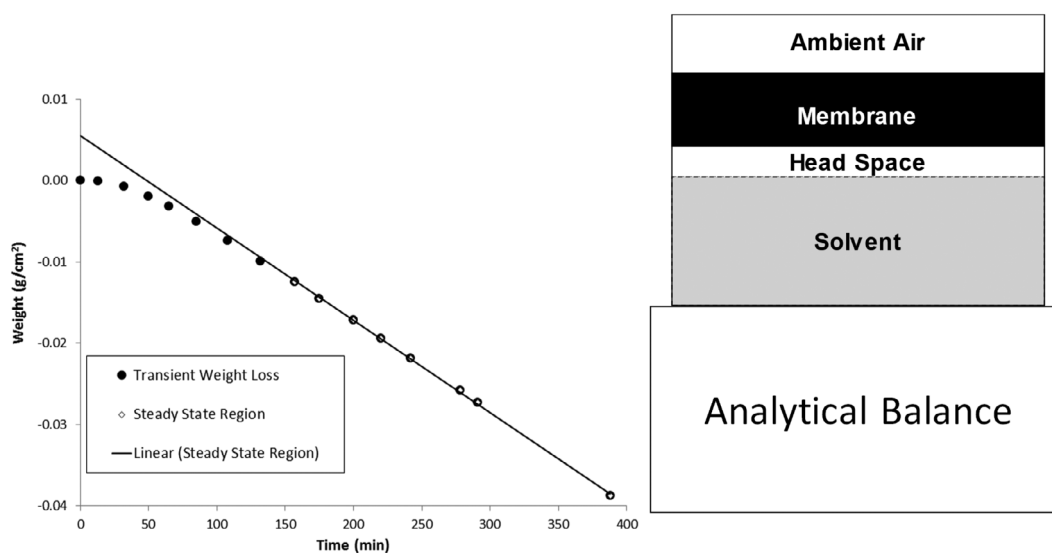


FIGURE 11 Comparison of pseudo-Payne cell desorption experiment performed with toluene and silicone rubber (Sample 2) at 25°C by measuring weight loss from a sample container. The data illustrate that diffusion can be observed during the transient measurement and that steady-state transmission can be seen in the long-term behavior

Despite the fact that the isotherm point evaluated from the desorption experiment was associated with 100% RP, the diffusion coefficient is assigned to an average solvent concentration within the membrane since transport occurs across the entire membrane and the concentration at the $x = 0$ face of the membrane is 11.1 wt% toluene while the face of the membrane at $x = L$ is maintained dry, that is, 0 wt% toluene. If measuring the diffusion rate versus solvent concentration is of interest, one should note that with the $x = 0$ surface maintained at 100% RP, a diffusion coefficient at a lower solvent concentration than about 4 wt% cannot be measured in this polymer/solvent system.

Since the outer surface of the membrane is already held at 0% RP, the only means by which to measure diffusion rates at lower solvent concentrations in the desorption experiment is to reduce the relative pressure inside the Payne cell. For water vapor transmission tests this can be accomplished by creating salt solutions which lower the mixture vapor pressure relative to that of pure water.²⁸ In this work, a mixture of adsorbent and toluene was introduced to the sorption cup which was known to create an atmosphere of 30% RP below the $x = 0$ surface of the membrane. Since it took only a short amount of time to obtain a steady-state weight loss profile, only a small amount of solvent was lost from the system. Based on analyses described previously²⁹, this amounted to a variation of 0.1% RP or a 0.05 mm Hg change in the driving force pressure.

A desorption experiment was performed in which the membrane was initially dry, that is, $C_{1p} = C_{2p} = 0 \text{ g/cm}^3$, the outer surface of the membrane at $x = L$ was exposed to 0% RP for the duration of the experiment ($C_2 = 0 \text{ g/cm}^3$), and the solvent concentration below $x = 0$ was maintained at 30% toluene relative pressure at 25°C. The two unknowns from the experiment are the equilibrium concentration of solvent within the membrane at $x = 0$, C_1 , and the diffusion coefficient, D . These were evaluated using Equation 13 and are included in Figures 9 and 10 as the lower concentration permeation points. The agreement between the isotherm and diffusion data measured by the standard gravimetric experiment and the permeation cell desorption experiment is excellent. The Payne cell as well as wet-cup and dry-cup (permeation cell) methods have been used to measure steady-state transmission rates and permeation coefficients.^{12–14} A comparison of the analytical model developed in this work to transient weight change data shows that both diffusion and solubility coefficients (isotherm data) can be measured accurately as well.

5 | CONCLUSION

Permeation equipment is generally available to examine gas transport processes, but instruments accessible to study solvent migration are rare. In this work solvent transmission has been shown to be readily measurable by Payne cell gravimetric measurements. An analytical model has been derived which facilitates the evaluation of diffusion coefficients and isotherm data from transient, Payne cell sorption experiments. The analytical expressions have been validated by a complementary, numerical analysis and have been used to analyze experimental data for two separate toluene-silicone rubber systems. These data were benchmarked against diffusion and isotherm results measured by standard gravimetric experiments and are found to be in excellent agreement. The analytical model has been shown to be applicable to examining transient, unsteady-state data measured by wet-cup or dry-cup permeation methods.

For the Payne cell adsorption experiment to be successful, the rate of uptake by the solid adsorbent must at least be an order of magnitude faster than the rate of transport through the membrane in order to maintain a constant driving force across the membrane. The toluene/silicone rubber system was selected as a case study, since, at ambient conditions it is a fast-diffusing, high-solubility system, which provided a significant challenge to the adsorbent solid (see Figure 1). The data measured using the Payne cell are in excellent agreement with the diffusion coefficients and isotherm data collected by traditional techniques, thereby providing confirmation of the experimental protocol and the analysis assumptions. Furthermore, if the adsorbent captures solvent vapor sufficiently quickly in a fast-transmitting system (e.g., toluene-silicone) the driving force across the membrane should be easier to maintain constant in slower transmitting systems.

For strongly absorbing gases/vapors, the Payne cell gravimetric measurement will indicate an immediate response upon exposure to the membrane due to sorption by the polymer. For weakly absorbing membranes, little response will be seen in the gravimetric experiment until there is transmission through the membrane and adsorption onto the solid adsorbent. This, however, does not make the Payne cell measurement insensitive for weakly absorbing systems.

The most common traditional schemes to measure diffusion and solubility coefficients, that is, gravimetric and manometric methods, are experimentally challenging when sorption levels are low. Permeation methods, however, have been successfully used to examine gas diffusion and solubility in polymer membranes since they involve measuring the time dependence of the *total mass of permeant transmitted through* a membrane which is

more easily measured than the *total mass of permeant absorbed* by the membrane. Permeation systems that allow for use of solvents, however, are less common. Use of a Payne cell enables one to use a gravimetric set-up, which is viable for either gases or solvent vapors. Since transmission analysis has been successful for gas solubility measurements, it is reasonable to propose that the Payne cell technique will be equally successful for low solubility, solvent systems.

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