Sequential Vapor Sorption of Additional Penetrants in Preswollen Polymers

LAURENT G. BONTOUX and DAVID S. SOANE,* *Department of Chemical Engineering, University of California, Berkeley, California 94720*

Synopsis

Uptake and removal of a second penetrant in polymer samples preexposed to another vapor dictate many industrially important processes. Both the kinetics and equilibrium sorption can be strongly affected by the presence of the first permeant in the polymeric matrices. A novel experimental setup was constructed to study penetrant uptake in sequence. Sorption of the second vapor took place while the partial vapor pressure of the first vapor was maintained, so that diffusion into the preswollen polymer approximated transport in a pseudobinary system. Polybutylene was chosen in this work to illustrate the capability of this versatile experimental system. Both the rate of diffusion and equilibrium sorption of the second vapor were found to depend on the prevailing composition of the preswollen polymer for all penetrant pairs studied.

INTRODUCTION

Diffusion and sorption of volatiles in polymers are the key to many important industrial processes. In the blending of polymers to form alloys, and the formation of suspensions, inks, adhesives, paints, etc., the multiple components in the final mixtures must often be dissolved in solvents and sometimes cosolvents. Dissolution, a critical step in mixing polymers, begins with penetration of small molecules into the polymers. Devolatilization and removal of residual monomers to produce high pure polymers also depend heavily on composition-sensitive transport properties. In the past, most studies were done by measuring penetrant uptake and desorption kinetics and equilibrium, one component at a time. However, many applications can be found where volatile uptake or desorption occurs in the presence of other permeants. Several specific examples will be cited to demonstrate the need to know the sorption/desorption behavior of multiple penetrants in polymers. The first is in the area of membrane separation. Here, common feed streams consist of multiple components. Membrane selectivity can be greatly affected by the exact composition of the feed stream being processed, if the membrane material is swollen by one or more of the components being separated. Therefore, by definition, membrane separation processes reflect the net behavior of multicomponent uptake and permeation. Literature in this area is exemplified by the references cited.[1-6]

A second application involves the removal of residual monomers or solvent from a polymer. If the residue is difficult to remove, the polymer can first be

---

*To whom correspondence should be addressed.

CCC 0021-8995/89/050915-08$04.00

saturated by a mobile and volatile penetrant, loosening the constraints on the residue and increasing its diffusivity in the mixed matrix. Once the residue is devolatilized, the easily removable swelling agent is then allowed to leave the system. Supercritical CO_2 can be used for this purpose. Here, both partition and mobility of small molecules in CO_2-swollen polymers are important properties, with the latter being particularly vital. This principle can be applied in reverse to introduce difficult-to-insert molecules into a CO_2-swollen network. Once the desired equilibrium state is achieved, CO_2 can be quickly flashed off by pressure lowering. The inserted molecules are trapped by the rapidly rigidifying polymer network. This is a practical method to introduce normally sparingly soluble dyestuffs into glassy polymers.

A third area of industrial application is the swelling and dissolution of polymeric thin films, most notably photoresists.[7] Developer solutions found in lithography are often mixtures. For the development of e-beam resists, mixtures comprising a solvent and a nonsolvent are employed to optimize contrast and resolution. Their competitive penetration into the resist films are essential to the success of lithographic development processes.

Another example of multicomponent permeation is the use of polymers as barriers, such as containers, packages, and water supply pipes. If the polymers are preswollen by other components found in the environment, contaminants that otherwise would take a very long time to penetrate the barriers could readily leach into the supply. Finally, in the preparation, transport, and surface application of suspensions, adhesives, paints, inks, etc., controlled sequential addition of solvents is critical to the ultimate success.

It is clear that in order to improve existing products and processes, one must establish a firm understanding of how the presence of a penetrant alters the polymer matrix, and in turn how the altered system affects subsequent transport of a second penetrant. To this end, we have built an experimental system based on a Cahn recording microbalance to obtain data on diffusivity and equilibrium sorption of volatiles into presaturated polymers. This paper provides the details of this versatile system and presents preliminary results on polybutylene and several permeant pairs.

EXPERIMENTAL SETUP

The system was designed to perform sorption tests on any sample up to 100 g. The operating temperature ranges from 5 to 45°C. The main components include the following: (1) weighing mechanism (microbalance), (2) thermostated housing (balance and sample chambers), (3) vapor delivery system, (4) vapor distribution system, and (5) evacuation system. Figure 1 shows a schematic of the complete system.

Weighing Mechanism

The weighing assembly is a Cahn 1000 recording balance in a glass belljar. The sample and a reference weight have identical geometries and are contained in identical hangdown tubes. Sample and reference are both wrapped around cylindrical baskets made of Nichrome wire. The dimensions of these
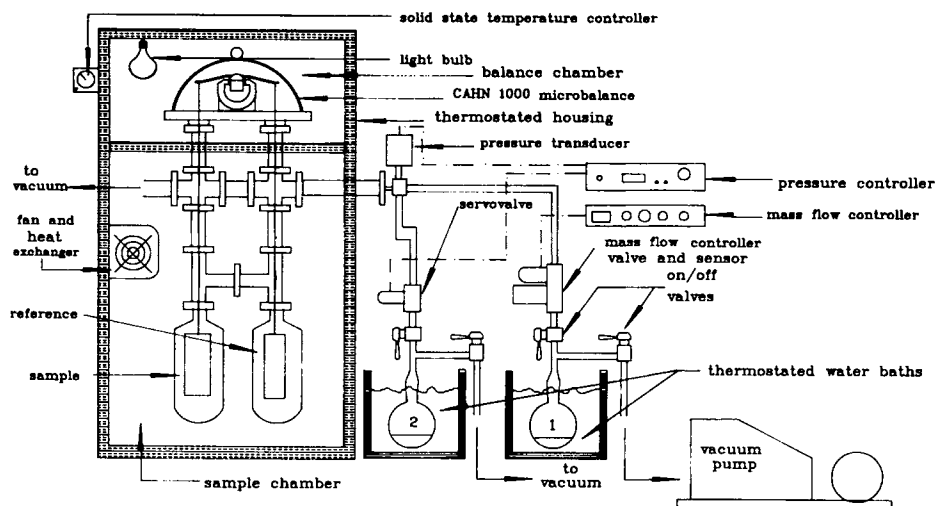
Fig. 1. Schematic of the sorption apparatus.

baskets are approximately 2.5 cm in diameter and 10 cm in length. The sample handling system is made as symmetrical as possible to avoid the effects of buoyancy and any nonuniformity of the environment. This entire balance and sample assembly is confined in a vacuum vessel made of glass and stainless steel.

The maximum sample weight allowed is 100 g, the maximum weight change that can be measured is 10 g, and the sensitivity of detection is 0.001 mg.

Thermostated Housing

A custom-made double thermostated housing is used to (1) ensure a constant temperature in the sorption area, (2) prevent condensation on the balance, and (3) independently control the temperature of the balance mechanism. This temperature control housing is composed of two chambers, one surrounding the balance mechanism, the other enclosing the hangdown tubes. The sample chamber has a two-pane double layer Plexiglas door to allow access to the hangdown tubes containing the sample and the reference. In the balance chamber, control is provided by a solid state controller connected to a thermocouple and a light bulb (heat source). For the sample, an aqueous solution of ethylene glycol from a thermostated bath is circulated into two heat exchangers (radiators). Heat exchange is efficiently promoted by two pancake fans.

The balance chamber contains only the weighing mechanism and can be kept at a temperature above that of the sample to avoid undesirable drifts due to temperature changes, and condensation of vapors on the beam and motor of the balance. This temperature in our experiments was kept at approximately 35°C. The sample compartment houses the hangdown tubes, the sample, and the reference. It is kept at the experimental temperature. In our case, this temperature was 20°C.

Vapor Delivery and Control System

The vapor delivery system is the innovative part of the whole system. It begins with two flasks containing the volatile chemicals to be studied. Both penetrants are in a liquid form, held in thermostated baths. The first flask is connected to the sorption chamber through a mass flow controller. The second is connected through a servo-valve operated by a pressure controller. A pressure transducer was installed in the tubing common to the two flasks. This tubing delivers the vapor mixture to the sample and reference. The hangdown bottles are two dead ends stopping the flow of vapors. However, both sample and reference tubes are connected to a vacuum source. Additionally, both penetrant flasks are connected (through a shutoff valve) to a vacuum pump in order to allow the degassing of the liquid chemicals without disturbing the sample compartment. The temperature in the water baths was kept above that of the sample to provide enough vapor pressure to obtain the desired vapor flow.

In actual runs, the first vapor was admitted in the sorption chamber at a desired constant pressure with the pressure controller off. The flow of vapor necessary to maintain that pressure was noted and regulated by means of a mass flow controller. After the first sorption equilibrium was reached, the pressure set point on the pressure controller was increased to a point equal to the initial constant pressure plus the desired partial pressure of the second component. This resulted in the second vapor entering the sorption chamber, with the partial vapor pressure of both components maintained constant throughout the experiment. Hence, this new vapor delivery and control system allows sequential sorption of a second permeant while the first one is kept present at a constant pressure.

Vapor / Gas Distribution System

This system is entirely built of 2-in. stainless steel tubing. Some sections are flexible for both convenience and dampening of the vibrations from the vacuum pump.

Evacuation System

The evacuation system is based on an Edwards dual-stage vacuum pump. This dual-stage mechanical pump can be used either by itself or as a primer for a downstream diffusion pump. The diffusion pump was only used occasionally for evacuation prior to a run. The vacuum attainable with the diffusion pump is 5×10^{-7} mm Hg and about 5×10^{-2} mm Hg with the mechanical pump alone.

A butterfly valve between the distribution system and the evacuation system is kept open when the sample needs to be desorbed. During the rest of the time, a metering needle valve controls the evacuation rate.

EXPERIMENTAL PROCEDURE

First, the system was evacuated and the sample desorbed completely. When a stable weight was reached, vapor from the first flask was admitted so as to yield the desired pressure. A complete sorption curve was recorded under

these conditions and the flow noted. The flow of the first chemical was kept constant and the pressure set point of the controller chosen at a level equal to the sum of the previous pressure and the additional pressure required to obtain the desired partial pressure of the second chemical. A second sorption curve was then recorded under these new conditions starting from the plateau weight at the end of the first one. Afterwards, the sample was desorbed and replaced prior to the next run.

The polymer used for this study was polybutylene. The samples were microtomed from commercial pipes used for water distribution. Penetrants were ethanol, n-hexane, and 1,2-dichloropropane, each as the first and then the second component (six combinations). Only one concentration of each was tested. The temperature of the runs was 20°C. At this temperature, the chosen delivery pressure of ethanol was 22 mm Hg, that of n-hexane 63 mm Hg, and that of 1,2-dichloropropane 21 mm Hg. This corresponds to relative pressures (P/P_{sat}) of 0.5 in all cases. One exception was made when n-hexane was the first component so as to avoid exceeding the saturation vapor pressure of the second component. Otherwise, it would be impossible to boil off the second component. In these two cases, the pressure of n-hexane was held at 20 mm Hg (16% of P_{sat}). However, the partition coefficient and diffusivity values reported for pure n-hexane were obtained at 0.5 P_{psat}.

Data Analysis

Two parameters of interest in this study of transport of organic vapors in polymers are the partition coefficient K and the diffusion coefficient D. K is a measure of the solubility of the permeant in the polymer. It is expressed as the ratio of the concentration of the organic chemical in the sample at equilibrium over its concentration in the surrounding atmosphere. At very low permeant pressures, the sample behaves linearly, and K is independent of pressure/concentration. However, when the prevailing partial vapor pressure is high, nonlinear responses can be elicited and K becomes a function of penetrant pressure. For glassy polymers, dual mode sorption is the dominant behavior. For rubbers, Henry's law or Flory's solubility usually provides an adequate description of the observed behavior. Diffusivity of organics in polymers is a very complicated subject.[8] For glasses, Case II, Super Case II, and other anomolous behavior have been reported, whereas, for rubbers, both concentration-dependent and concentration-independent Fickian diffusion are possible. At very low penetrant activities, even glasses may exhibit Fickian diffusion.

For our sample, the diffusion coefficient can be calculated using a solution of Fick's second law. In the case of a thin film and for a constant diffusion coefficient, a good approximation is $D = 0.049 \, L^2/t_{hS}$, where L is the sample thickness and t_{hS} is the half-sorption time.[8] We justify the use of this equation by the fact that the pressure steps are of modest magnitude. Besides, we are only interested in qualitative trends in this preliminary work to test the feasibility of our newly designed experimental system. One may argue that for the diffusion of organic chemicals into polymers, D is usually not constant but is a function of concentration. For reasons of simplicity, the above equation will be used to calculate the average diffusion coefficient representing the concentration range of each run.
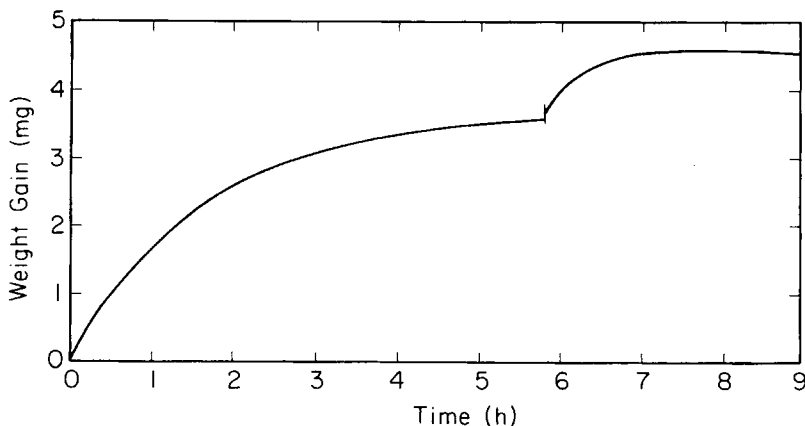
Fig. 2. Output traces for a 6.5-μm-thick microtomed polybutylene sample. The first state sorption corresponds to exposure to 20 mm Hg of *n*-hexane. In the second stage, ethanol is added, while the total pressure is kept at 44 mm Hg.

RESULTS AND DISCUSSION

Typical output traces are in the form of a two-stage sorption curve (Fig. 2). The first stage corresponds to exposure to a pure permeant and the second one to binary penetrants, simultaneously.

Tables I and II summarize the diffusion and partition coefficients from the various runs. The value for the pure chemical is used as a reference to indicate any change associated with the presence of the first penetrant.

As can be seen from Table I, the partition coefficients become greater when the sample has previously been exposed to another chemical, except in the case of ethanol after exposure to *n*-hexane. When *n*-hexane is introduced as the second permeant, in both cases of presaturation by ethanol and dichloropropane, the change incurred is rather small. On the other hand, ethanol and dichloropropane uptake are both significantly assisted by the presence of the other component of the pair. Surprisingly, dichloropropane uptake is also increased by the preexposure to *n*-hexane.

The diffusion rates do not seem to be affected in the same manner as the partition coefficients. In the case of *n*-hexane and 1,2-dichloropropane, each seems to exert a great deal of influence on the other. A very polar first component (ethanol) slows down the penetration of the polymer by hexane, however.

TABLE I
Second-Stage Partition Coefficients at 20°C for Ethanol, 1,2-Dichloropropane, and *n*-Hexane
in PB after Exposure of the Sample to the First Penetrant

First component	Second component		
	Ethanol	Dichloropropane	*n*-Hexane
Ethanol	32[a]	220	74
Dichloropropane	104	125[a]	63
n-Hexane	30	175	59[a]

[a] These values are for the pure chemicals at 0.5 P_{sat}.

TABLE II

Second-Stage Diffusion Coefficients (10^{-10} cm^2/s) for Ethanol, 1,2-Dichloropropane, and n-Hexane in PB after Exposure of the Sample to the First Permeant at 20°C

First component	Second component		
	Ethanol	Dichloropropane	n-Hexane
Ethanol	6.9[a]	3.7	9.1
Dichloropropane	9.6	3.9[a]	21
n-Hexane	25	10	9.8[a]

[a] These values are averages between 0 and 0.5 P_{sat}.

Based on the above preliminary results, we have been able to demonstrate the potential utility of gravimetric technique. The use of this experimental system allows ready calculation of the diffusion coefficient and partition coefficient of the first chemical in the usual manner. The diffusion coefficient of the second chemical in the impregnated sample and an estimate of the partition coefficient of the second chemical in the preswollen sample can then be calculated assuming the measured weight gain to be due entirely to the second component in the second stage of weight gain.

During the second stage of a run, there is no easy way to check independently that the partial pressure of the first chemical in the ambient mixture indeed remains at the same level as during the first stage. However, variations, if any, will be minimal, since the same flowrate of vapor is admitted into the sample chamber as before and the evacuation rate stays constant as well.

A more serious concern is that the experiment does not detect if any of the first chemical is displaced by the sorption of the second one. In other words, one is not certain if there is as much of component 1 in the sample at the end of the second stage as at the end of the first stage. In case the concentration of component 1 is not held constant in the polymer, the partition coefficient obtained for component 2 is only apparent and not necessarily the true value.

In conclusion, this short study provides a brief glimpse of the complexity of the behavior of polymers in contact with multiple penetrants. The current plan involves a systematic study of the concentration dependence of the interactions of the pairs in a given polymer. Prediction of successive sorption curves produced by a system similar to the one presented here is in principle possible with any number of components. This would require quantitative knowledge of pairwise interaction parameters. Repeated runs of the sort presented in this preliminary work would generate a large enough data base for modeling use.

The ultimate refinement of this technique may involve monitoring of the relative concentrations of components 1 and 2 in the sample during the second stage of sorption to ensure that the observed weight gains due to each component are strictly additive. Perhaps spectroscopic measurements can be used in conjunction with this gravimetric technique.

References

1. R. C. Binnings, R. G. Lee, J. F. Jennings, and E. C. Martin, *Ind. Eng. Chem.*, **53**, 45 (1961).
2. J. W. Reilly, E. J. Henley, and H. K. Staffin, *AIChE J.*, **16**, 353 (1970).
3. M. H. V. Mulder and C. A. Smolders, *Sep. Purif. Methods*, **15**, 1 (1986).
4. R. Rautenbach and R. Albrecht, *J. Membr. Sci.*, **25**, 1, 25 (1985).
5. K. C. O'Brien and W. J. Koros, *J. Membr. Sci.*, **29**, 229 (1986).
6. E. S. Sanders and W. J. Koros, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 175 (1986).
7. J. S. Papanu, D. W. Hess, D. S. Soane, and A. T. Bell, *J. Electrochem. Soc.*, to appear.
8. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Clarendon, Oxford, 1975.