Effect of Pressure on CO_2 Transport in Poly(ethylene Terephthalate)

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Synopsis

The CO_2 solubility, permeability, and diffusion time lag in poly(ethylene terephthalate) are reported at 35° and 65°C for CO_2 pressures ranging from 0.07 to 20 atm. The subatmospheric time lag and permeability measurements were made with a glass system at North Carolina State University, while the measurements between 1 and 20 atmospheres, using an identical polymer sample, were made at The University of Texas with a metal system capable of tolerating gauge pressures up to 30 atm. The measured solubility, permeability, and time lag all show strong deviations from the well-known simple expressions for gases in rubbery polymers. The solubility isotherm is nonlinear in pressure, and both θ and P are quite pressure dependent, with each showing tendencies to approach low and high pressure asymptotic limits. These effects decrease as temperature increases and would be expected to disappear at or near the glass transition where the amorphous regions become rubbery. The importance of reporting the pressure levels used in transport measurements is emphasized for gas/glassy polymer systems where transport process do not follow linear laws.

INTRODUCTION

The simplest model for gas sorption and permeation in polymers envisions the equilibrium sorption isotherm to follow Henry's law,

$$C = k_D p \tag{1}$$

and the transport to follow Fick's first law with a concentration-independent diffusion coefficient[1] D. In this case, the resulting differential equations which describe both transient and steady-state transport processes are linear; and, as a result, it is possible to define and measure simple parameters which are independent of the external pressure boundary conditions. The most common and useful of these are the permeability P and time lag θ, which for the above-mentioned model are related to fundamental quantities via

$$P = k_D D \tag{2}$$

$$\theta = l^2/6D \tag{3}$$

Both P and θ can be deduced from a single transient permeation experiment,[2] thus giving k_D and D provided the membrane thickness l is known. Generally, the experiment is done with a very high vacuum on the downstream side of the

2899

membrane while a finite driving pressure, p_2, is used upstream. For the simple model described above, which is evidently quite valid for rubbery polymers, the value of p_2 selected for this experiment should not matter, and usually its range is dictated by details of equipment design while the exact value is selected to provide a convenient rate of gas transmission. Because of this presumed independence of the measured parameters on this pressure, it has become common practice to not even report it.

There is substantial evidence, however, that this simple model is inadequate for a number of gas/glassy polymer systems. For example, there are now many published sorption isotherms which show substantial nonlinear behavior even at modest or low pressures.[3-22] Theoretical interpretation of these results has led to models that suggest either P or θ or both might depend on p_2.[23,24] Some recent data for CO_2 in polycarbonate have shown[22] that P and θ both depend on p_2. These data were obtained with a permeation apparatus designed specifically for the purpose of varying p_2 in rather high ranges. The upstream side of the equipment must, therefore, be a rather robust metal design and construction. Such equipment is not well suited for measurements with p_2 much below atmospheric pressure because small air leaks may contaminate the upstream compartment which was designed to contain high gas pressures. Conversely, small outward leaks are of no concern when operating as a high-pressure cell. As a result, the earlier polycarbonate/CO_2 data do not extend below 1 atm, although there is considerable evidence for this system and others presently being studied that P and θ may show considerable pressure dependence below 1 atm. In general, there may not be a practical low-pressure range where it is always safe to assume pressure independence of these measured parameters.

Most laboratories equipped for gas permeation research use equipment constructed entirely of glass, and consequently p_2 is restricted to subatmospheric values. Therefore, if one chooses to study the effect of p_2 on the transport parameters, these equipment design considerations restrict most investigators to cover the range below 1 atm although it would be desirable to cover the entire range in some instances. A joint project was, therefore, carried out to measure P and θ as a function of p_2 on the same polymer sample over a broad pressure range traversing 1 atm. The laboratories at North Carolina State University and The University of Texas which are well equipped for measurements with p_2 below and above 1 atm, respectively, cooperated in this project. Results for the system poly(ethylene terephthalate)/CO_2 at 35° and 65°C are reported here.

The data presented are intended to demonstrate the effect of upstream pressure on P and θ for systems in which transport processes are not described by linear differential equations. Presently, there is evidence which suggests that all gas/glassy polymer systems fall into this category. The results will not be analyzed or discussed extensively in terms of any specific model; however, such an analysis is now underway for this same system using much more extensive data and will be reported in a later paper.

EXPERIMENTAL

Permeation

The apparatus and operating procedures for both the low-pressure and high-pressure experiments used in this study have been described in the litera-

ture.[22,27] Both cells used large downstream gas receiver volumes and a sensitive MKS Baratron as the downstream pressure sensor to permit maintenance of a very small pressure as the boundary condition at the downstream membrane face. The vacuum system at North Carolina State was constructed of glass, while the system at The University of Texas was constructed of metal to permit application of upstream driving pressures up to 30 atm.

For the high-pressure system, the diffusion area was determined ($\pm 2\%$) by masking both membrane faces with either vapor-deposited aluminum or carefully cut aluminum foil tape. To seal against high pressures without imposing undue stress on the glassy membrane, it was convenient to adopt a double-sealing arrangement. A piece of filter paper, cut to the same size as the unmasked diffusion area, was placed on the sintered metal support to facilitate gas flow to the downstream receiver. The membrane was then adhered to the bottom metal plate with an epoxy resin, and a good vacuum seal was easily achieved. To seal against high-pressure leaks to the outside from the cell top, a Teflon gasket with sufficiently large inside diameter was placed on the metal plate so that it surrounded, but did not contact, the epoxy–membrane assembly. The gasket was compressed by tightening six symmetrically placed nuts. This double-seal system has proven to be adequate in fairly high temperature and pressure service. Degassing times at least ten times longer than the largest observed time lag were used between runs. The time lag was not affected by more protracted degassing.

For the low-pressure system, standard sealing techniques and previously reported operating procedures[27] worked well.

Sorption

Design and operation of the sorption cell are described elsewhere.[21] The cell was a dual-volume, dual-transducer design similar to that reported in an earlier paper[22] with modifications to improve the signal-to-noise ratio.

RESULTS

Poly(ethylene terephthalate) (PET) was selected for this work because of its potential importance in carbonated beverage packaging[25] and its strongly non-linear sorption behavior.[7,14,15,19] The particular sample chosen was a commercially available 2-mil film which is optically quite transparent although very crystalline. More detailed characterization of this polymer is available elsewhere.[26]

The PET/CO$_2$ sorption isotherms measured in The University of Texas laboratories at 35° and 65°C are presented in Figure 1. It is clear that these isotherms are quite nonlinear and cannot be described by Henry's law; however, they can be accurately described by, and understood in terms of, the dual sorption model[3,9] extensively discussed in the literature.[6–25] From these sorption results, various models[9,23,24] would predict either or both the permeability and the time lag to depend on pressure.

Figures 2 and 3 show the time lag and permeability plotted versus the upstream CO$_2$ pressure for a range of approximately 3.5 decades of pressure. Note that both θ and P are pressure dependent as expected. The solid data points ($p_2 > 1$ atm) were obtained in The University of Texas laboratories, while the open
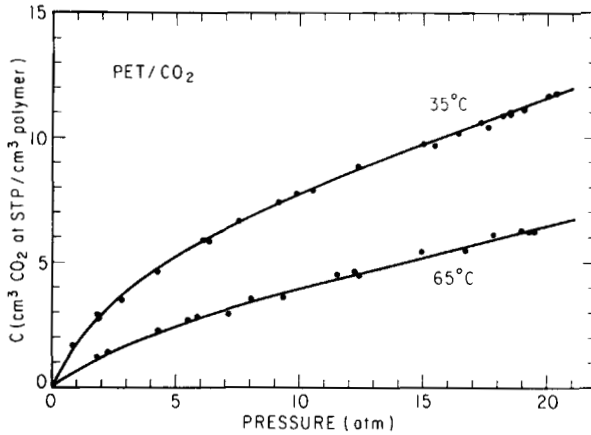
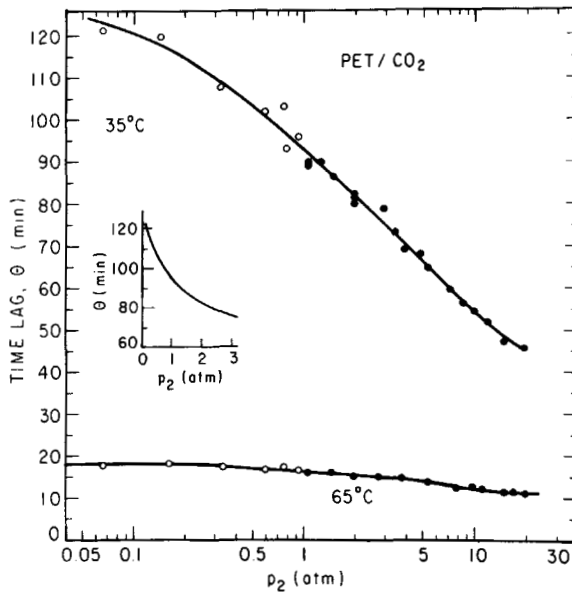Fig. 1. CO_2 sorption isotherms for poly(ethylene terephthalate).

Fig. 2. Effect of upstream CO_2 pressure on diffusion time lag for a 2.0-mil poly(ethylene tereph-thalate) membrane. Note the logarithmetic scale employed to allow displaying the wide range of upstream CO_2 pressures used. The smoothed 35°C data are plotted on the insert with arithmetic pressure coordinates to show the strong pressure effect on θ near and below atmospheric pressure.

points ($p_2 < 1$ atm) were obtained in the North Carolina State University laboratories using an identical specimen. It is gratifying to see the excellent agreement between the two sets of data obtained using equipment of quite different designs.

DISCUSSION

It is clear from Figure 1 that the amount of sorption is a strongly nonlinear function of pressure and decreases with increasing temperature. There is con-
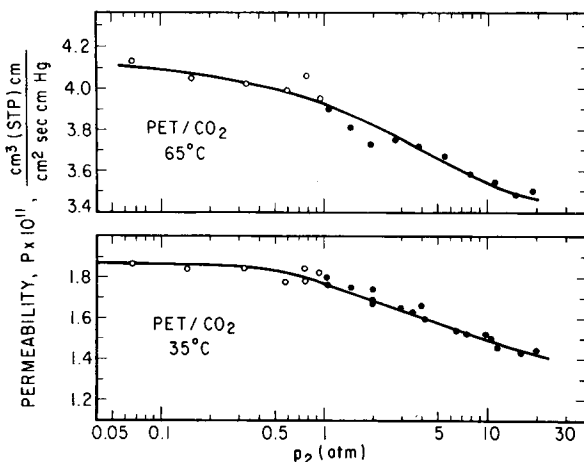
Fig. 3. Effect of upstream CO_2 pressure on permeability. Note that on a percentage basis the pressure effect on permeability is larger at 35°C (23% change between 0.07 and 20 atm) than at 65°C (16% change between 0.07 and 20 atm).

siderably less curvature in the isotherm at 65°C than at 35°C. These nonlinear sorption isotherms preclude both the use of Henry's law to describe sorption and the use of the combined set of eqs. (2) and (3) for the experimental transport parameters θ and P.

The results presented in Figure 2 indicate, especially at 35°C, a pronounced effect of p_2 on θ. In fact, these data show no pressure range in which the time lag is reasonably constant. Considerably different values of D would be reported by investigators working at different driving pressures if eq. (3) were casually applied. As the temperature is raised, the magnitude of the time lag decreases as one expects, and the pressure dependence of the time lag is also decreased. For example, at 35°C, θ changes by 63% over the pressure range shown, while at 65°C, this change is only 39%.

The permeability at 65°C is more than a factor of 2 higher than the permeability at 35°C, and the pressure dependence of the permeability is greater at 35°C than 65°C. Although this reduction in pressure effect is less dramatic for the permeability than for the time lag, it is still significant. These observations are gratifyingly consistent with a theory that attributes pressure dependence of θ and P and the nonlinear nature of the sorption isotherm to dual sorption mechanisms which seem to be characteristic of the glassy state.[24] This theory predicts that both θ and P have zero-pressure and high-pressure limits, and Figures 2 and 3 seem to be consistent with this notion. The insert plot on Figure 2 of θ versus pressure on arithmetic coordinates at 35°C shows more vividly the strong pressure dependence between zero and 1 atm.

Presumably, as the temperature approaches the glass transition, the complex relationships responsible for these observed pressure dependences should degenerate into the simple relationships for gases in rubbers given by eqs. (1)–(3). Complete interpretation of these data and additional data spanning the glass transition of PET (about 80°C), in terms of the theoretical models mentioned, is in progress and will be reported in a later paper.

The preceding discussion and data emphasize the value of reporting the pressure at which gas/glassy polymer transport measurements are made.

Moreover, the simple expressions which are adequate to describe sorption and transport of gases in rubbery polymers should not, in general, be used for the more complex case of gases in glassy polymers.

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