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TREATMENT OF ANOMALOUS VAPOR DIFFUSION IN POLYMERS

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Abstract

The mechanics of thermally-activated gaseous diffusion in polymers have long been studied for development of theoretical understanding of the interactive forces responsible for the non-linear nature of diffusion and the resultant enthalpic changes in the polymer. Methodologies and calculations have been developed in this work for treatment of experimental data for elimination of thickness-related anomalies in water vapor diffusion and for delineation of pressure effects. Linearized data for different polymer thicknesses and the attendant internal thermal effects have been generated by using calculated single molecule diffusion values. Equally linear data are obtained for different pressures by the use of a graphical method from which identical diffusion values are obtained, independent of material thickness and external pressure. True comparisons and classification of polymers as to their diffusivities are thus possible for development of barrier materials for food and drug packaging and for protective encapsulation of electronic devices.

Results will be reported for three structurally different polymers.

Keywords: barrier materials, internal thermal effect, non-linear diffusion, single molecule diffusion, vapor/solid ratio

Introduction

Various aspects of the non-linear nature of moisture transport through the heterogeneous morphology of polymer structures as well as the mechanics of thermally-activated moisture vapor diffusion in polymers have been the subject of several studies [1–7]. Graham [8] was perhaps the first to observe that the course of vapor diffusion through polymer network proceeds first by condensation to the liquid followed by evaporation to the gaseous state, thus establishing the direct role of temperature as a driving force in steady-state diffusion. The diffusion mechanism developed by Frisch [9] relates the size of the diffusing molecules to pre-existing holes or spaces in the polymer chain conformation throughout the polymer diffusion boundary or thickness. This followed from the idea by Cohen and Turnbull [10] that only a few large holes of a size comparable to those of the molecules contribute to directional diffusional mobility. Departure from this con-

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formity is the prime reason for thickness-related anomalous vapor diffusion in polymers. Since this mobility depends on the polymer's structural conformity with the internal stress created by the pressure differential across the polymer thickness, the role of external pressure must also be considered. Some other stress factors affecting diffusion in polymers have been evaluated [11]. Diffusional non-linearity with respect to material thickness has been attributed by Crank and Park [1] to anomalous diffusion effects resulting from structural inhomogeneities. Shewmon [12] has correlated diffusional anomalies with the stress factors of volume anisotropy in solid materials. The purpose of this paper is to demonstrate for the first time the usefulness of the application of single molecule diffusion, calculated from experimental data, for treatment of anomalous vapor diffusion in structurally different polymers. This method produces a linear relationship between diffusion and material thickness and can also be used for generation of linear data for internal thermal effects during diffusion. Moreover, a graphical method will be presented for determination of diffusion values free of pressure effects and independent of thickness. Such determinations can afford true comparison and classification of polymers as to their diffusivities for development of effective barrier materials.

Water, water vapor and organic vapor all differ in their diffusion characteristics through polymers. Only water vapor will be considered in this work.

Theoretical

Thermal parameters

Temperature plays an important role in vapor diffusion in polymers. Diffusion is found to increase with increasing temperature, but more importantly, activation energy requirement determines the magnitude of diffusion [13, 14].

If the diffusion process is visualized as occurring over a period of time in discrete steps, following a meandering pathway through the polymer network, the motion must continually decay in the absence of any energy input. The contribution of temperature as a driving force can generally be evaluated from determination of activation energy over a temperature range. Thus, different polymer types can be classified as to their vapor diffusivity. It is apparent, however, that a certain amount of work will be performed on the polymer by the thermally-activated diffusion process. Nevertheless, the contribution of thermal energy at any given moment to the total kinetic energy of diffusion is difficult to assign, since mechanical energy of fluid eddies also contribute to the total energy. As a practical means, the ratio of temperature-induced vapor uptake to unit areas of different thicknesses of a polymer can be calculated from internal thermal effects for alternative evaluation of this relationship, as described below.

Internal thermal effects

Internal thermal effects in diffusion result directly from thickness-related non-linearity. According to Crank [15], diffusion proceeds both by transfer of vapor and by transfer of heat. The mechanism can be interpreted as follows:

As vapor starts to initially diffuse through the pores of the polymer at constant temperature, some of the diffusants become temporarily immobilized due to structural hindrance. This leads to condensation and evolution or absorption of heat. If heat is given up in the process, an increase in surface temperature occurs from loss of heat from the internal volume of the polymer. This will cause a decrease in further vapor propagation inside the polymer. A temporary equilibrium will be reached in which the uptake of vapor at the modified temperature will be in equilibrium with the external vapor pressure. For small temperature differences, heat is lost by radiation and convection in direct proportion to temperature over the surrounding. As internal cooling proceeds and surface temperature increases, the uptake of vapor proceeds again. This description is in complete accord with experiments carried out by King & Cassie [16]. The influence of hygrothermal effect in moisture transport for some polymers containing varying percentages of hydrophobic silicone moiety has been studied [17].

In the above situation, the uptake of vapor and the heat flow are symmetrical about the central plane of the polymer thickness, bounded by $x=0$ to $x=L$, where L is the thickness of the polymer. At $x=1/2L$, the differential heat of condensation (ΔH/g cal) with time can be expressed as:

$$\Delta H=1/2\rho L_{\mathrm{V}}\,(\mathrm{d}R/\mathrm{d}t)$$

where L_{V} is the latent heat of vaporization of water/cal g^{-1}, ρ is the mass/g of the polymer and t denotes time/s. R represents the vapor/solid ratio i.e. the mass of vapor taken up for the mass of polymer used/g.

$$R=B(t/L^2)^{1/2};\ L \text{ is the polymer thickness}$$

B/g cm $\mathrm{s}^{1/2}$, is calculated from experimental results:

$$B=4\,C_0\,(D/\pi)^{1/2}$$

where C_0 is the value of steady state diffusion/g, and D is the average diffusion coefficient/cm^2 s^{-1}, for the concentration range of 0 to C_0 of vapor.

(dR/dt) reduces to R/g at infinite time i.e. at steady state.

The above equations provide a means of calculating the change in enthalpy during the process of diffusion and thus for evaluating R.

The derivations of the units are as follows:

$$B=\mathrm{g}\{(\mathrm{cm}^2\ \mathrm{s}^{-1})/(\mathrm{number})\}^{1/2}=\mathrm{g\ cm\ s}^{-1/2}$$

$$R=\mathrm{g\ cm\ s}^{-1/2}(\mathrm{s\ cm}^{-2})^{1/2}=\mathrm{g}$$

$$\Delta H=\mathrm{g\ cal\ g}^{-1}\ \mathrm{g}=\mathrm{g\ cal}$$

In keeping with the conventional practice in permeability measurements, steady-state diffusion values of water vapor/ml, were extrapolated to 24 h for 100 in^2/645.16 cm^2 of polymer surface at 1 atm pressure. The diffusion values are expressed in volume of vapor referenced to a calibration factor of $1.094\cdot10^{-4}$ of vapor at 100°C and 1 atm for 0.1 μl of water injection. The conversion factor for volume of water/ml, to mass of water/g, is $7.904\cdot10^{-4}$. Sample thickness was measured in ml/$2.54\cdot10^{-3}$ cm.

Delineation of pressure

Unoccupied spaces exist between various chain segments in polymer structures and larger spaces are formed due to thermally activated segmental chain mobility. In the normal diffusion process of a vapor into a polymer of sufficient thickness, the polymer experiences differential compression and expansion in localized areas due to uneven stresses [18] as the vapor diffuses through the various depths of the polymer. An increase in head pressure will tend to increase compression more than expansion and diffusivity has been found to decrease with increasing pressure for the polymers studied in this work. A graphical technique for use of an equation, devised by the author, will be used here for delineation of pressure effects.

The equation has the form:

$$p/\{V_t(p-p_0)\}=(p_0/p)\{(C-1)/C\}+1/C$$

where p=applied head pressure (known), p_0=post-diffusion pressure (atmospheric), V_t=steady state diffusion value (determined), C=concentration of vapor at experimental pressure (evaluated).

Plot of the left side of the equation *vs.* p_0/p produces a straight line whose slope is $x=(C-1)/C$ and its intercept on the ordinate is $y=1/C$. At zero pressure, $V_t=1/(x+y)$.

Treatment of non-linear diffusion

The most significant outcome of this work is that thickness-related non-linear diffusion data can be linearized on molecular basis using the Avogadro theorem. The method consists of first converting the vapor diffusion value per unit thickness (V_t mil^{-1}) to the number of equivalent gm moles and then to the number of molecules. Single molecule diffusion value (V_t') is then calculated by dividing the measured diffusion value (V_t) by the calculated number of molecules.

Experimental

A schematic of the laboratory-designed (non-commercial) experimental setup is shown in Fig. 1. The unit consists of (1) a controlled carrier gas stream flowing through a gas-tight sample cell; (2) a septum-capped inlet for injection of water into the gas stream; (3) a heated-line inlet for introduction of water vapor into the sample cell; (4) a four-way valve system for isolation of components 2 and 3; (5) a thermistor-pair detector cell; and (6) a bridge power supply for controlling detector current and sensitivity.

The sample cell and its attendant gas flow system are housed in a thermostatically controlled oven.

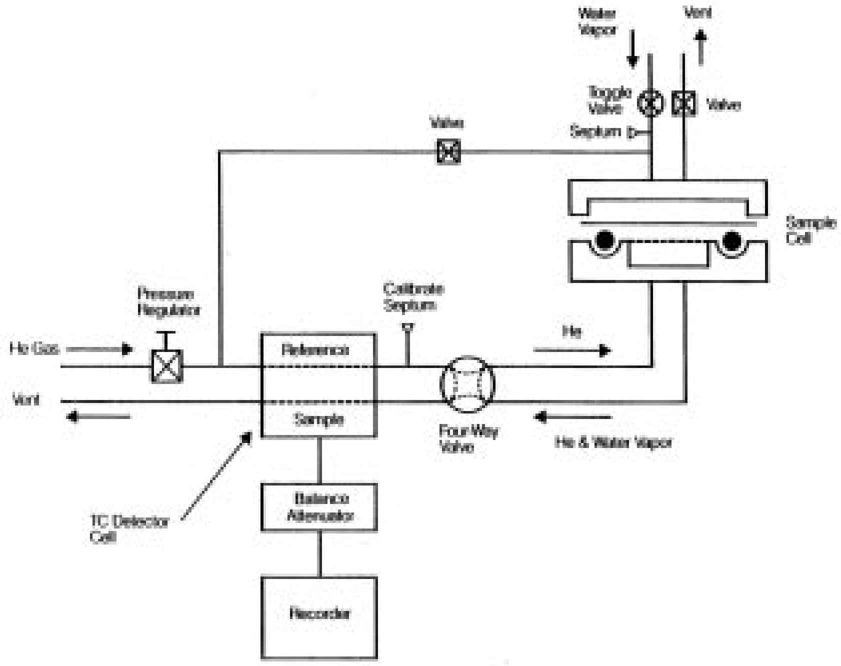

Fig. 1 Schematic of diffusion measuring apparatus

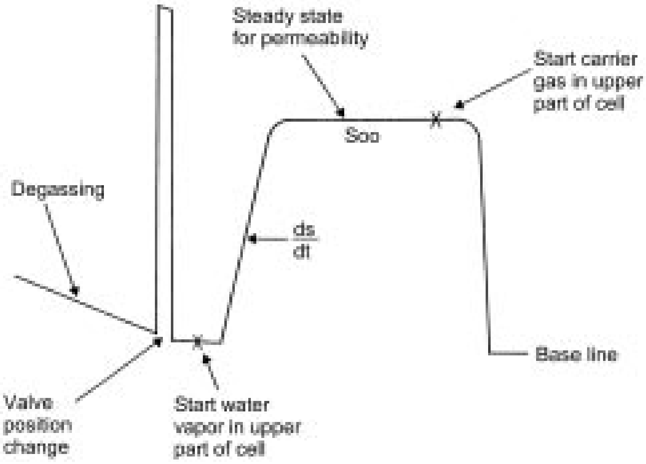

Fig. 2 Schematic representation of water vapor diffusion curve

The detector cell was kept at a high enough temperature to avoid condensation of water vapor, but low enough so as not to reduce sensitivity.

A standard chart recorder was used to obtain a record of detector response. A schematic representation of a typical water vapor diffusion curve is shown in Fig. 2.

Method

The polymer sample of known thickness in the form of a disc, measuring 4 inches in diameter, was clamped into the sample cell and equilibrated isothermally within the test chamber at a constant carrier gas (helium) flow rate. Water vapor was generated in a flask connected to the cell with a heated line. The reference area used in calcula-

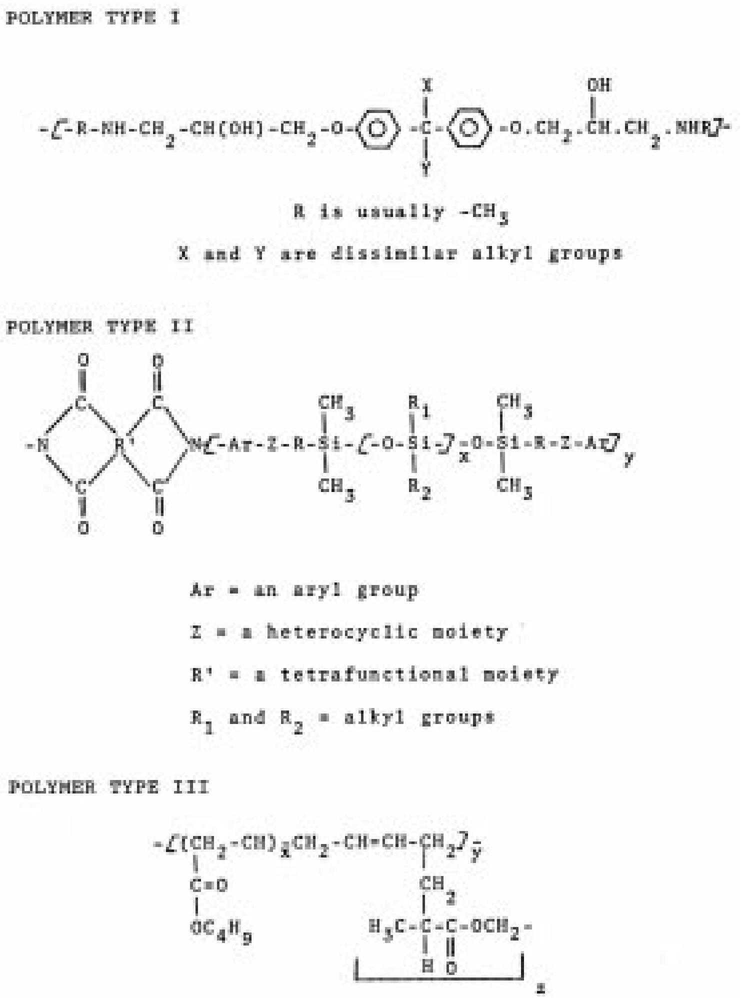

Fig. 3 Polymer structures of test samples

tion was averaged from two groups of ten injections of 0.5 μl of water. The relative standard deviation of each group was found to be 0.01%. All reported values for steady state diffusion (V_t) were averaged from at least 3 determinations.

Technique

All valves were kept open except the toggle valve for water vapor during sample conditioning at a constant temperature of 100°C. The four-way valve was positioned to purge the entire system when the carrier gas flow was turned on. After complete degassing when a stable baseline was obtained, the four-way valve was turned to isolate the sample cell from the water injection system, but the upper cavity of the sample cell was allowed to continue to be purged. When a stable baseline was obtained again after the valve change, injections were made for reference area. The valve was turned again to purge the entire system till a stable baseline was obtained. The carrier gas to the upper cavity of the sample cell was shut off and water vapor was introduced to adequately fill the top part of the cell. The water vapor toggle switch and vent were kept closed to retain water vapor in the sample cell. A steady rise in baseline indicates onset of diffusion. After steady state diffusion (S_∞) in Fig. 2 is reached, the valves are opened when the signal returns to the baseline.

Test samples

Results for three structurally different polymers are shown in Fig. 3. These polymers are hydrophobic and swelling is not a factor.

Results and discussion

The three parameters in the mechanics of vapor diffusion, viz. (1) molecular basis (V_t molecule^{-1}, designated $V_{t'}$), (2) differential heat of condensation (ΔH) and (3) the vapor/solid ratio (R) were examined. Diffusion data at 100°C for all three polymers are given in Table 1.

Although diffusion values are clearly not linear with corresponding sample thickness, plots of single molecule diffusion against respective thickness, shown in Figs 4–6, bear linear relationship for all three polymers.

As previously stated, steady state diffusion is preceeded by stepwise ingress of vapor accompanied by changes in the heat of condensation (ΔH) which is dependent on the vapor/solid ratio (R). Linearized relationships are obtained for both these quantities when these are plotted *vs.* molecular diffusion for each polymer type (Figs 7–9). The use of molecular diffusion is thus further justified for obtaining linearized values for true comparisons between different polymers. Figs 10–12 are included here to show normal diffusion behavior of these polymers with respect to temperature. The dependence of the magnitude of diffusion on the activation energy, determined from Arrhenius plots are given in Table 2.

Table 1 Experimentally obtained and calculated diffusion data

Sample thickness/ mil and cm	Steady-state diffusion for stated thickness/ ml(100 in^2)$^{-1}$(24 h atm)$^{-1}$	V_t mil^{-1}/ same	V_t molecule^{-1} same
POLYMER TYPE I			
$23.9/60.703\cdot10^{-3}$	$8.30\cdot10^{3}$	$3.47\cdot10^{2}$	$8.91\cdot10^{-19}$
$25.5/64.770\cdot10^{-3}$	$8.60\cdot10^{3}$	$3.37\cdot10^{2}$	$9.50\cdot10^{-19}$
$26.9/68.326\cdot10^{-3}$	$6.40\cdot10^{3}$	$2.38\cdot10^{2}$	$1.00\cdot10^{-19}$
$27.5/69.850\cdot10^{-3}$	$3.80\cdot10^{3}$	$1.38\cdot10^{2}$	$1.02\cdot10^{-18}$
$28.0/71.120\cdot10^{-3}$	$5.30\cdot10^{3}$	$1.89\cdot10^{2}$	$1.04\cdot10^{-18}$
$28.3/71.882\cdot10^{-3}$	$6.26\cdot10^{3}$	$2.21\cdot10^{2}$	$1.05\cdot10^{-18}$
POLYMER TYPE II			
$9.0/22.86\cdot10^{-3}$	$8.37\cdot10^{4}$	$9.30\cdot10^{3}$	$3.35\cdot10^{-19}$
$10.0/25.40\cdot10^{-3}$	$8.00\cdot10^{4}$	$8.00\cdot10^{3}$	$3.72\cdot10^{-19}$
$12.5/31.75\cdot10^{-3}$	$7.50\cdot10^{4}$	$6.00\cdot10^{3}$	$4.65\cdot10^{-19}$
$14.0/35.56\cdot10^{-3}$	$7.20\cdot10^{4}$	$5.14\cdot10^{3}$	$5.52\cdot10^{-19}$
$15.0/38.10\cdot10^{-3}$	$4.96\cdot10^{4}$	$3.31\cdot10^{3}$	$5.58\cdot10^{-19}$
$18.0/45.72\cdot10^{-3}$	$5.02\cdot10^{4}$	$2.79\cdot10^{3}$	$6.70\cdot10^{-19}$
POLYMER TYPE III			
$8.7/22.098\cdot10^{-3}$	$3.89\cdot10^{5}$	$4.47\cdot10^{4}$	$3.24\cdot10^{-19}$
$12.3/31.242\cdot10^{-3}$	$4.05\cdot10^{5}$	$3.29\cdot10^{4}$	$4.58\cdot10^{-19}$
$15.0/38.100\cdot10^{-3}$	$4.78\cdot10^{5}$	$3.19\cdot10^{4}$	$5.58\cdot10^{-19}$
$18.2/46.228\cdot10^{-3}$	$5.26\cdot10^{5}$	$2.89\cdot10^{4}$	$6.78\cdot10^{-19}$
$20.9/53.086\cdot10^{-3}$	$3.68\cdot10^{5}$	$1.76\cdot10^{4}$	$7.78\cdot10^{-19}$
$21.0/53.340\cdot10^{-3}$	$3.91\cdot10^{5}$	$1.86\cdot10^{4}$	$8.27\cdot10^{-19}$

Table 2 Activation energy *vs.* diffusion

Sample thickness/ mil and cm	Activation energy/kcal	Diffusion at 100°C/ ml(100 in^2)$^{-1}$ (24 h atm)$^{-1}$
Type I		
$28.7/72.898\cdot10^{-3}$	2.7	$6.26\cdot10^{3}$
Type II		
$9.0/22.860\cdot10^{-3}$	3.93	$8.37\cdot10^{3}$
Type III		
$20.9/53.086\cdot10^{-3}$	6.08	$3.68\cdot10^{5}$

Finally, Fig. 13 illustrates the interpolated zero pressure diffusion values for three different thicknesses of polymer type II, determined under head pressures of 1086, 1357, 1682, 1900 and 2171 psi (7487.693, 9356.169, 11224.64, 13100.02 and 14968.49 KPa respectively). Calculated values from these plots are given in Table 3 which show that the same diffusion value is obtained for all three thicknesses.

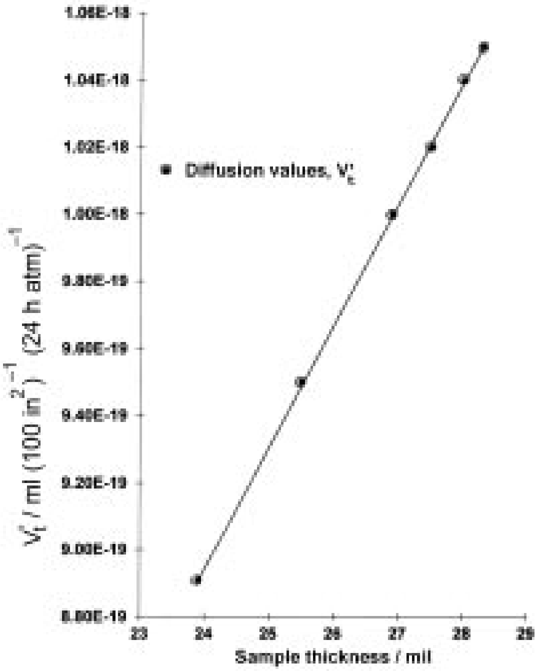

Fig. 4 Single molecule diffusion for polymer type I. • – Diffusion values, V_t'

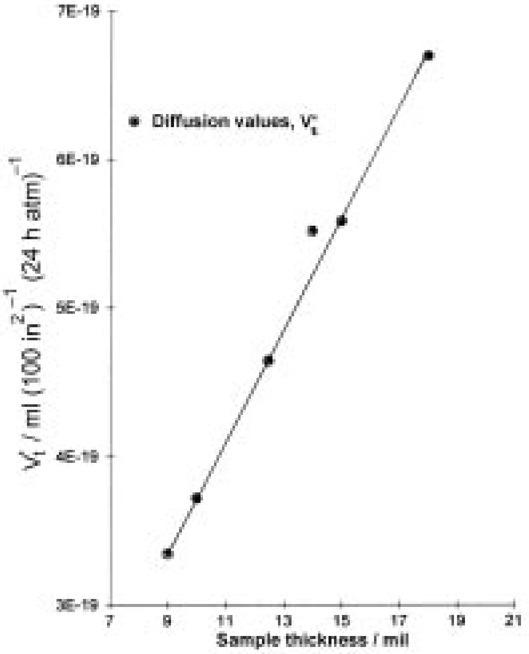

Fig. 5 Single molecule diffusion for polymer type II. • – Diffusion values, V_t'

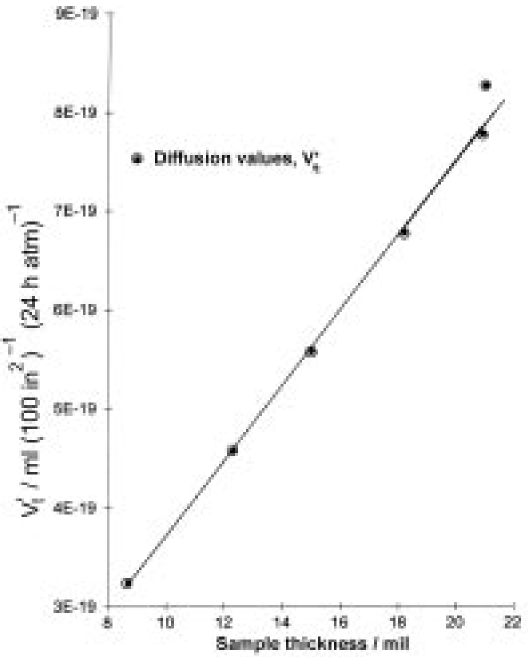

Fig. 6 Single molecule diffusion for polymer type III. • – Diffusion values, V_t'

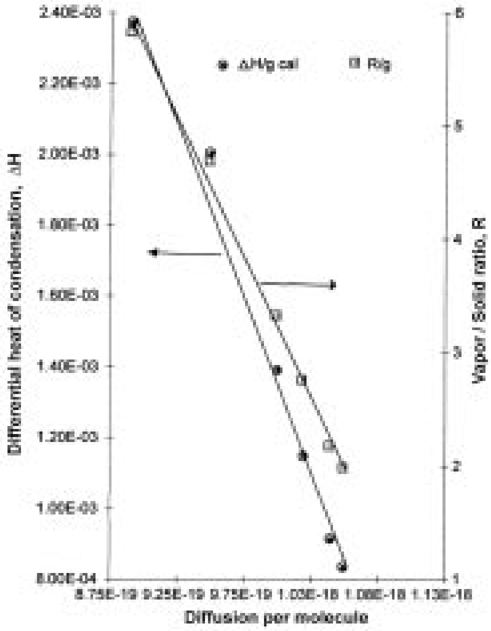

Fig. 7 Internal thermal effects in diffusion for polymer type I

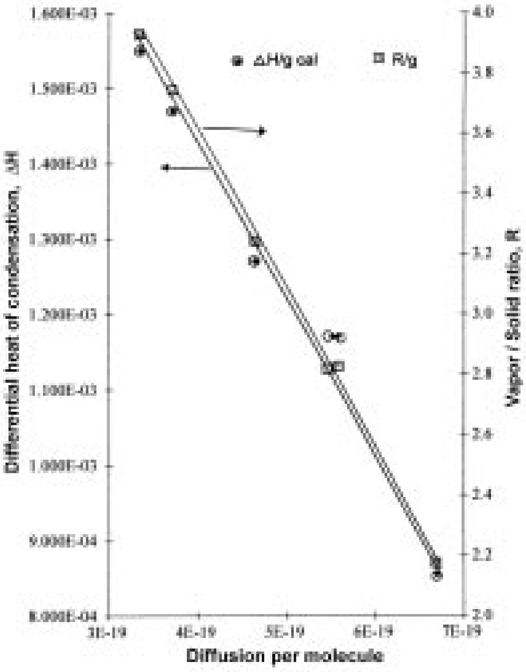

Fig. 8 Internal thermal effects in diffusion for polymer type II

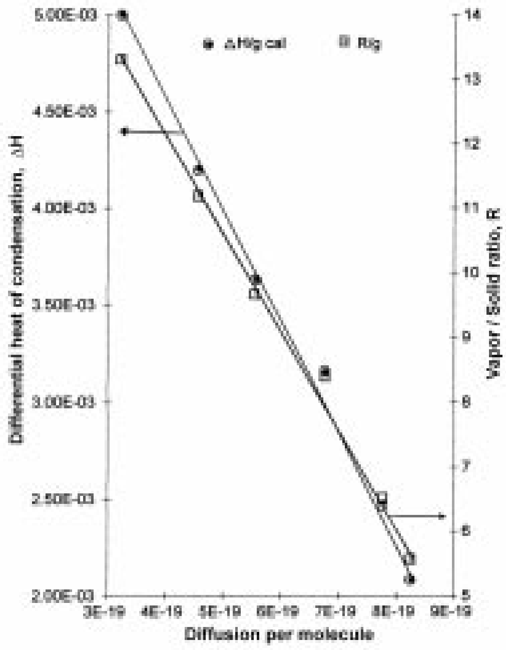

Fig. 9 Internal thermal effects in diffusion for polymer type III

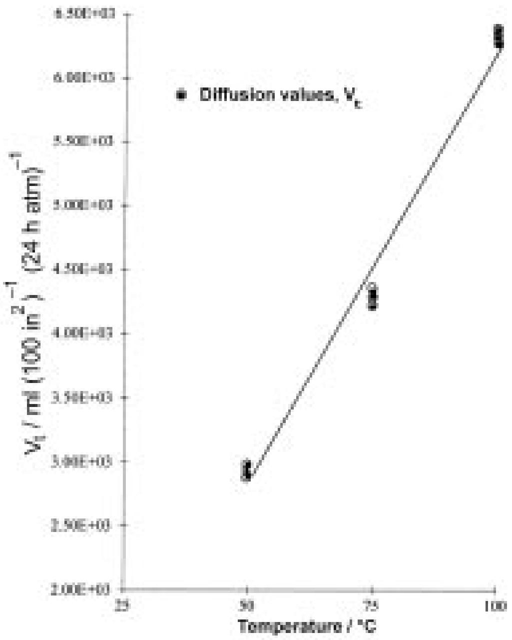

Fig. 10 Diffusion *vs.* temperature for polymer type I. • – Diffusion values, V_t

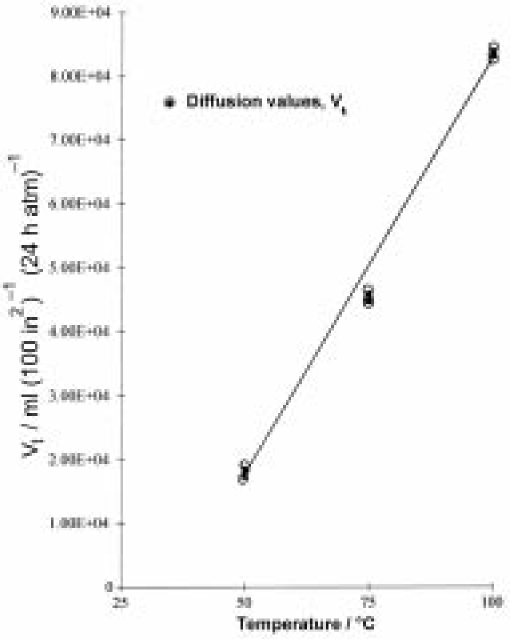

Fig. 11 Diffusion *vs.* temperature for polymer type II. • – Diffusion values, V_t

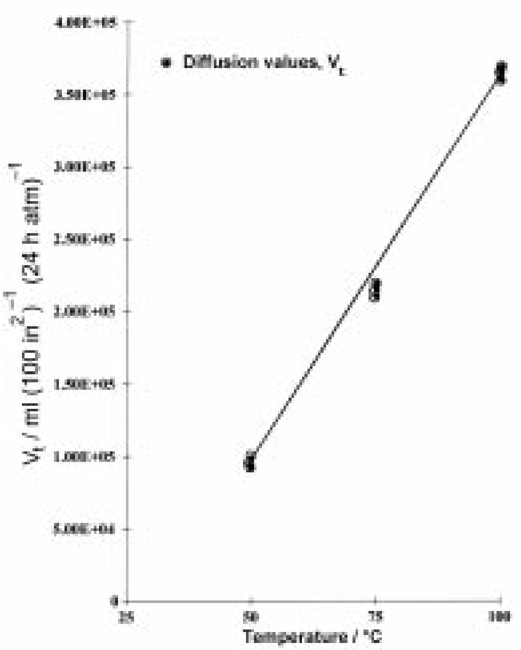

Fig. 12 Diffusion *vs.* temperature for polymer type III. • – Diffusion values, V_t

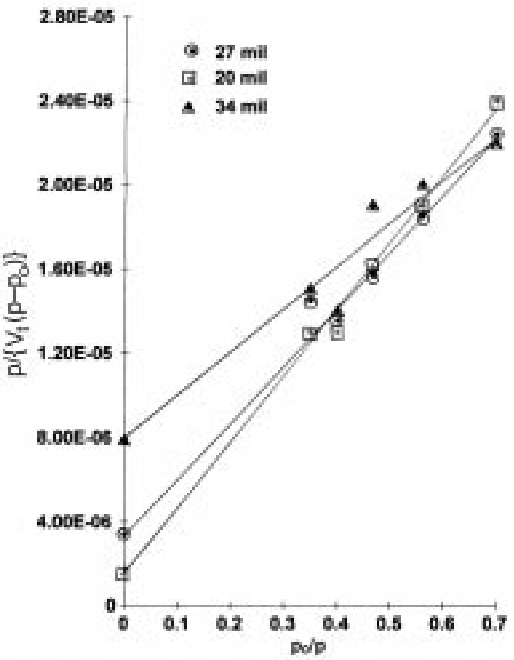

Fig. 13 Diffusion at various pressures for polymer type II

Table 3 Diffusion values at zero pressure (Fig. 13)

Sample	Slope	Intercept	V_t
A (27.0 mil)	$2.86\cdot10^{-5}$	$0.34\cdot10^{-5}$	$3.12\cdot10^{4}$
B (20.0 mil)	$3.06\cdot10^{-5}$	$0.15\cdot10^{-5}$	$3.12\cdot10^{4}$
C (34.0 mil)	$2.42\cdot10^{-5}$	$0.78\cdot10^{-5}$	$3.12\cdot10^{4}$

Conclusions

The mode of non-linear diffusion through polymer thickness has been discussed in this paper. Conventional experimental methods have been used for diffusion data. A treatment has been proposed for linearization of experimental data based on calculated single molecule diffusion, independent of material thickness and a graphical method has been presented for delineation of external pressure effect. The methodology can be useful for obtaining data for true comparison between polymers with respect to their vapor diffusivity. Such comparisons are necessary for the development and classification of polymers as vapor barrier materials.

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