

Sorption of lower alcohols in poly(ethylene terephthalate)

Preeti Chandra, William J. Koros*

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

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ABSTRACT

This paper presents equilibrium sorption and kinetics of lower alcohols in a 1.5 μ thick, biaxially oriented PET film. Methanol, ethanol, *n*-propanol and iso-propanol have been studied for the solubility and sorption kinetics in this film to understand how these properties change with penetrant size and branching. It is observed that *n*-propanol shows dual mode characteristics at all activities whereas the other three penetrants show Flory–Huggins uptake at high activities. Infinite dilution solubility is estimated and compared with that of esters, ketones and other hydrocarbons previously reported. The dispersive solubility parameter, δ_d is found to correlate well with the solubility of penetrants with the same functional group. The hydrogen bonding parameter, δ_h is observed to influence the solubility of penetrants with the same carbon number but different functional groups. This correlation with the solubility parameters may be extended to other functional groups and used to predict the infinite dilution solubility of larger penetrants in PET. Diffusion coefficients in the Fickian kinetics regime and Berens–Hopfenberg parameters in the non-Fickian kinetics regime have been evaluated. Diffusivity increases with concentration and decreases with size. Diffusion coefficient of iso-propanol is an order of magnitude lower than that of *n*-propanol due to branching effects.

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1. Introduction

Poly(ethylene terephthalate) (PET) is a well known barrier material used for packaging of food, dairy products and beverages such as carbonated drinks, beer, juices. Growth in the packaged foods and beverages market has led to growth in the market for PET as well. In these products, retention of taste imparted by the flavor molecules is of great importance. The flavor is lost either due to flavor scalping or chemical degradation. To estimate the extent of flavor scalping, knowledge of the transport properties of the species is essential. However, measurement of the transport properties of flavor molecules, which are large organic compounds, is difficult due to the low diffusivities, which translate into very long experiment times [1]. As a result, actual flavor molecules are much less studied and development of predictive capabilities gains significance. A potential route to prediction is the correlation of transport properties of small organic species in PET with their physical properties and subsequent extrapolation to larger molecules. Researchers have reported the solubility and diffusivity of a series of organic molecules such as linear and branched alkanes (*n*-butane, *i*-butane, *n*-pentane and *i*-pentane), linear and branched ketones (acetone, methyl ethyl ketone, methyl isopropyl ketone

and methyl *n*-propyl ketone), linear esters (ethyl acetate and methyl acetate), acetaldehyde, benzene and toluene at different penetrant activities in biaxially oriented, semicrystalline PET. Solubility and diffusivity of liquid methanol, acetone, dimethyl formamide, dioxane and methylene chloride have also been studied [1–7]. Correlation of solubility and diffusivity of these penetrants with critical constants has been proposed by Dhoot and coworkers [1]. Upon examination of the correlation of solubility with critical temperature or Lennard–Jones force constant, it was observed that the properties of the polar molecules deviate significantly from the fit which may lead to large inaccuracies in the solubility estimation. It is, therefore desirable to develop another correlation which will allow better estimation of the properties of polar, condensable molecules [1,8].

This paper presents systematic study of equilibrium sorption and kinetics of lower alcohols in the 1.5 μ thick, biaxially oriented PET film. Methanol, ethanol, *n*-propanol and iso-propanol have been studied for the solubility and sorption kinetics in this film to understand how these properties change with increasing size of the penetrant and how branching may influence them. Sorption isotherms and kinetics have been discussed and correlation of the penetrant solubility with various thermodynamic constants has been investigated to understand the structure property relationships of small interacting penetrants. Quantities that have the best correlation and may be used for prediction purposes have been proposed.

* Corresponding author. Tel.: +1 404 385 2845; fax: +1 404 385 2683.

E-mail address: wkoros@chbe.gatech.edu (W.J. Koros).

2. Experimental

2.1. Materials characterization

A biaxially oriented, semicrystalline PET, $1.5 \pm 0.15 \mu$ thick film, procured from GoodFellow Co., was used in this study. (Devon, PA). Methanol (99.9% ACS grade), ethanol (anhydrous, 99.5%), 1-propanol ($\geq 99.80\%$) and 2-propanol (anhydrous 99.5%) were purchased from Sigma–Aldrich for the sorption experiments. Table 1 shows some relevant properties of the penetrants.

The density of the film, obtained using a density gradient column (Techné™, Burlington, NJ) filled with calcium nitrate–water solution was measured to be 1.3914 g/cc. The crystalline weight fraction was calculated from the sample density (ρ) using the two-phase model represented in equation (1). The amorphous phase density (ρ_a) is taken to be 1.331 g/cc and the density of PET crystals (ρ_c) is taken to be 1.455 g/cc [9], resulting in estimated crystalline fraction of 51%.

$$X_c = \left(\frac{\rho - \rho_a}{\rho_c - \rho_a} \right) \frac{\rho_c}{\rho} \quad (1)$$

Crystallinity was also calculated to be 51% using wide angle X-ray diffraction studies which were performed on a Rigaku Micro Max 002 system. Cu K α X-ray source with Ni filter was used. Glass transition temperature was measured using differential scanning calorimetry performed DSC 220C from Seiko Instruments (Horsham, PA). First scans at a heating rate of 10 °C/min were taken. Glass transition occurred at 79 °C is close to the T_g of PET, usually reported between 70 and 85 °C. Melting temperature (T_m) of 257 °C also matches well with the typically reported T_m of 245–265 °C. Crystallinity was also estimated from DSC and was found to be lower at 31%. This may be attributed to the difference in the measurement observed using different techniques such as DSC, WAXD etc. Literature references and a discussion of this observation are provided in [10].

2.2. Gravimetric vapor sorption

Equilibrium uptake and kinetics were measured at 35 °C using the McBain quartz spring apparatus [11]. Details of the experimental setup and the measurement methodology are discussed previously [10]. The isotherms are obtained using the integral sorption method. Sorption kinetics is obtained by recording the spring position at different times after introduction of the vapor at time $t = 0$. Equilibrium is assumed to be attained when the spring position does not change over the course of 24 h. Once equilibrium is reached, the pressure is increased by introducing more vapors during sorption. The concentration of methanol in the polymer (C , ccSTP/ccpoly) is calculated using equation (2).

$$C = \left(\frac{K\Delta x}{g} \right) \frac{22414 \times \rho_p}{M_W \times M_p} \quad (2)$$

Table 1

Properties of lower alcohols and PET solubility parameter.

Property \rightarrow , Penetrant \downarrow	Saturation vapor pressure at 35 °C, mmHg [33]	Molar volume, cc/mol	Critical temperature, K	Solubility parameter, MPa ^{1/2}			
				δ_d	δ_p	δ_h	δ
Methanol [13]	202.3	40.7	518	15.1	12.3	22.3	29.7
Ethanol [13]	103.3	58.5	521	15.8	8.8	19.4	26.6
<i>n</i> -Propanol [13]	36.0	75.2	513	16.0	6.8	17.4	24.6
<i>i</i> -Propanol [13]	80.0	68.4	541.7	15.8	6.1	16.4	23.5
PET [34]	–	–	–	19.4	3.5	8.6	21.5

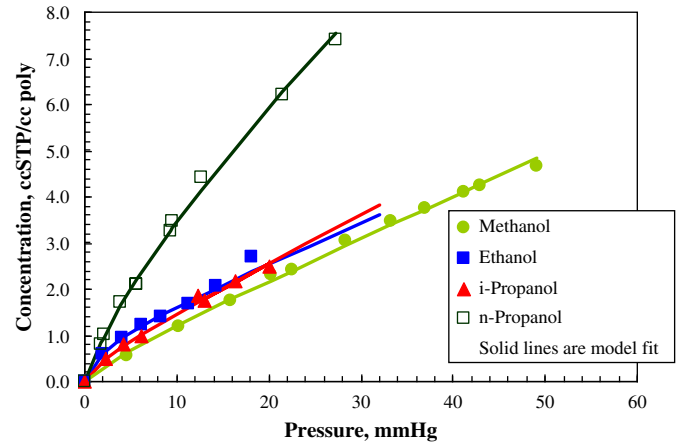


Fig. 1. Dual mode region of the sorption isotherm of MeOH, EtOH, *i*-PrOH and *n*-PrOH.

K (g/s²) is the calibration constant of the spring, g (cm/s²) is the rate of acceleration due to gravity, Δx (cm) is the change in spring position, ρ_p (g/cc) is the polymer density, M_p (g) is the mass of the polymer sample hung on the spring, M_W is the molecular weight of the penetrant.

3. Results and discussion

3.1. Equilibrium sorption at low activities – dual model regime

In the low activity region, ethanol (EtOH) and iso-propanol (*i*-PrOH) show dual mode behavior (i.e. the isotherm is concave to the x -axis) up to an activity of 0.18 and 0.35 respectively. The dual mode model is a phenomenological theory according to which sorption in glassy polymers occurs in two domains, a non-equilibrium Langmuir's domain or 'holes' where microvoids of excess free volume are frozen in and, an equilibrium domain or Henry's Law region. It is represented by equation (3) below. C_H is the saturation capacity of these holes, b is the affinity constant, and p is the pressure of the penetrant outside the polymer, C is the penetrant concentration in the polymer and k_D is Henry's Law solubility constant.

$$C = \frac{C_H b p}{(1 + b p)} + k_D p \quad (3)$$

It has been shown previously by the authors that methanol (MeOH) uptake in 15.2 μ m non-annealed semicrystalline, biaxially oriented PET follows dual mode model at low activities. Positive deviation from the dual mode model occurs at $p/p_0 = 0.25$ [12]. p is the partial pressure of the vapor and p_0 is the saturation vapor pressure at 35 °C. The overall isotherm of methanol and the physical properties of the thin biaxially oriented film are very similar to those of the thicker, non-annealed film [12]. The isotherms of the lower alcohols and the corresponding dual mode model fit are shown in Fig. 1. *N*-propanol (*n*-PrOH) shows dual mode

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