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Measuring and correlating diffusivity in polymer–solvent systems using free-volume theory

Ronald P. Danner*

Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, United States

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ABSTRACT

This paper provides a review of the measurement, data reduction, and correlation of diffusivities using the free-volume theory for polymer–solvent systems, particularly in the range of very low solvent concentration. The experimental methods discussed are inverse gas chromatography, gravimetric sorption, and pressure decay. The free-volume model is described in terms of its potential and limitations for correlation and extrapolation of diffusion data. Data are given and analyzed for a number of systems including two of practical importance: solvents in poly(vinyl alcohol) and bisphenol-A in poly(vinyl chloride).

1. Introduction

In the design of typical chemical operations dealing with liquid or gas systems, the diffusivities of the components are generally not very important, i.e., diffusivities are not a limiting factor in the process. For polymer–solvent systems, however, the diffusivities often are very important and can significantly affect the operation or safety. Table 1 provides the first clue as to why this is true.

The diffusivity of gases and liquids in polymers are many orders of magnitude slower than in normal gas or liquid systems and are much stronger functions of concentration and temperature. Furthermore, these extremities occur in the range of low solvent concentration. A typical example of the temperature dependence is shown in Fig. 1 for the toluene-poly(vinyl acetate) system in the infinitely dilute solvent range. Over the 90 °C temperature range the diffusivity changes by six orders of magnitude. While the infinite dilution concentration may at first appear to be of little interest, it is extremely important in many applications in terms of the property of the polymer, health standards, and safety. Frequently the concentrations of residual monomers and solvents in a polymer are required to be reduced to a few parts per million. When the diffusivity gets into the range of 10^{-8} cm^2/s or less it will take a long time to reduce the concentration to the required limit. Belt dryers must be long and run slowly, batch driers must have long hold up times, etc. Knowledge of the temperature and concentration dependencies of the diffusivity therefore becomes a key component of the process design.

Fig. 2 demonstrates the concentration dependence of the diffusivity of toluene in poly(vinyl acetate). At 80 °C the diffusivity varies over three orders of magnitude as the concentration increases from zero to just 30%. There are numerous areas where there is an important coupling of thermodynamics and diffusion: polymerization reactions; formation of films, coatings, membranes and foams; controlling morphology; membrane technology, barrier films; plastic recycling; controlled drug release; electronics; and so on. In this paper the primary focus is on how to best measure and correlate the diffusion in the very low concentration range.

2. Measurement techniques

There are many ways to determine diffusivities in polymer–solvent systems. They can roughly be divided into sorption techniques, chromatographic, and a catch-all other group. Direct sorption (or desorption) methods include gravimetric [1], pressure decay [2], and piezoelectric crystal [3]. Weighing the uptake (or release) of the solvent using either a spring quartz balance or an electronic balance has been the source of the great majority of data. The pressure decay method is used less but can be applied over large temperature and pressure ranges. Piezoelectric crystals have been used the least probably because of the experimental difficulties encountered in the procedure. Inverse gas chromatograph has been widely used to determine the infinite dilution characteristics: partition and diffusion coefficients. It

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* Tel.: +1 814 863 4814; fax: +1 814 865 7846.
E-mail address: rpd@psu.edu

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Table 1
Characteristics of binary diffusion coefficients.

Type of system	Order of magnitude (cm^2/s)	Concentration–temperature dependence
Gas–gas or gas–vapor	0.1–1.0	Very weak
Gas–liquid	$\sim 10^{-5}$	Weak
Normal liquids	10^{-5}–10^{-6}	±100%
Polymer solutions	10^{-5}–10^{-8}	±1000%
Gas or liquid in polymer liquid or polymer solid	10^{-12}	Factor of 1000

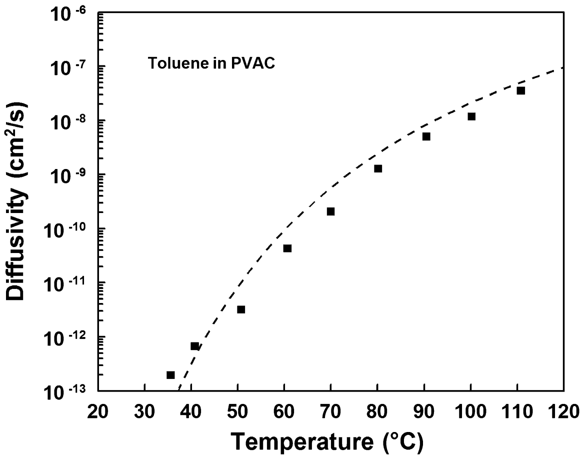

Fig. 1. Diffusivity of toluene in poly(vinyl acetate) at infinite dilution (dotted line is referenced in Section 3).

can, however, also be applied to finite concentrations [4]. The other methods include membrane and permeation cells, light scattering, and NMR. Each of these has unique characteristics and applications. In this paper the focus is on the approaches that have more general, practical applications – gravimetric, pressure decay, and inverse gas chromatography.

2.1. Sorption methods

Sorption methods have certainly provided most of the diffusivity data for polymer–solvent systems – the direct gravimetric method outweighing the pressure decay method by far. The old-fashioned gravimetric apparatus used a quartz spring and simply measured the change in the spring length as the polymer absorbed or desorbed solvent. In general these apparatuses were limited to atmospheric pressure or less. The modern gravimetric approach is to use an electronic balance which measures the weight through a magnetic coupling. This allows the measurements to be made over wide ranges of temperature and pressure. The pressure decay method uses an indirect way of determining the change in solvent concentration in the polymer. The polymer is enclosed in a constant temperature, constant volume chamber and a known initial pressure of solvent is admitted to the system. The change in pressure with time is measured and then through an equation of state the mass of solvent lost (or gained) in the vapor space is determined. In either case the equilibrium state determines the equilibrium solubility and the unsteady state period is used to determine the diffusivity. The key to the latter is the application of Fick's second law.

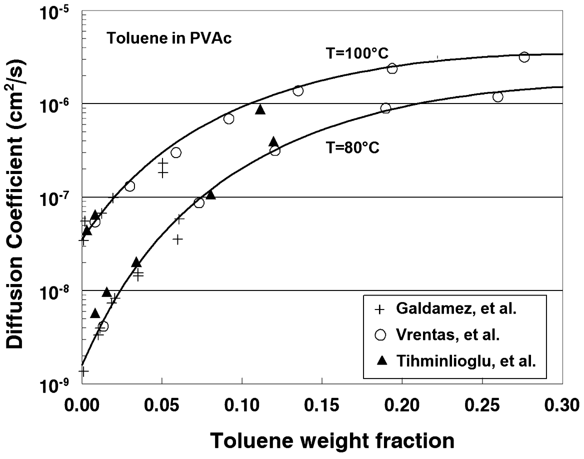

Fig. 2. Diffusivity of toluene in poly(vinyl acetate) at finite concentrations. Curves are free-volume regressions of each temperature independently.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial \ell^2} \tag{1}$$

Here D is the diffusion coefficient, C is the solvent concentration, ℓ is the diffusion distance (for a film, the thickness or half the thickness; for a sphere, the radius, R_p), and t is the time. The boundary conditions are typically $C = 0$ at $t = 0$; C = equilibrium concentration at the surface for $t > 0$, and $\partial C/\partial x = 0$ at the center of the film or sphere for $t \geq 0$. The well-known solutions to this set of equations have been given by Crank [5]. For films:

$$\frac{M_t}{M_\infty} = 2\left[\frac{Dt}{\ell^2}\right]^{1/2}\left[\pi^{-1/2} + 2\sum_{n=1}^{\infty}(-1)^n \mathit{ierf}\left(\frac{n\ell}{2\sqrt{Dt}}\right)\right] \tag{2}$$

and for spheres:

$$\frac{M_t}{M_\infty} = 6\left[\frac{Dt}{R_p^2}\right]^{1/2}\left[\pi^{-1/2} + 2\sum_{n=1}^{\infty} \mathit{ierf}\left(\frac{nR_p}{\sqrt{Dt}}\right)\right] - 3\frac{Dt}{R_p^2} \tag{3}$$

Here M is the mass uptake at any time (t) or at equilibrium (∞) For small times the last terms in these equations become negligible. Rearranging for films:

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{\pi\ell^2}\right)^{1/2} \quad \text{or} \quad \frac{M_t/M_\infty}{\sqrt{t}} = 2\left(\frac{D}{\pi\ell^2}\right)^{1/2} \tag{4}$$

and for spheres:

$$\frac{M_t}{M_\infty} = 6\left(\frac{Dt}{\pi R_p^2}\right)^{1/2} \quad \text{or} \quad \frac{M_t/M_\infty}{\sqrt{t}} = 6\left(\frac{D}{\pi R_p^2}\right)^{1/2} \tag{5}$$

These equations provide the diffusion coefficients based on the initial slope of a plot of the square root of time versus M_t/M_∞. A typical uptake curve is depicted in Fig. 3. The use of this approach requires a number of assumptions:

1. No swelling (constant thickness)
2. No edge effects (one-dimensional diffusion)
3. No concentration dependence of D over the range of the experiment
4. Constant temperature

Although it is a bit more difficult one can also fit the entire curve to Eq. (2) or (3). The choice depends upon the accuracy and availability of the data.

2.2. Inverse gas chromatography

The inverse gas chromatography (IGC) method is primarily used to determine the partition coefficient (concentration in the polymer divided by the concentration in the vapor phase) and the diffusion coefficient at infinite dilution. This extreme limit is valuable