

# OPTIMIZATION OF FREE-VOLUME THEORY PARAMETERS FOR TERNARY POLYMERIC COATINGS FROM BINARY WEIGHT LOSS EXPERIMENTS

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In this work free-volume parameters needed for poly(styrene) – p-xylene-tetrahydrofuran coating and poly(methylmethacrylate) – tetrahydrofuran – ethylbenzene coatings were estimated by minimizing the difference between model predicted residual solvent and experimental residual solvent in binary coatings. Each ternary system needs two binary systems for example poly (styrene)-p-xylene-tetrahydrofuran system needs poly(styrene)-p-xylene and poly(styrene) – tetrahydrofuran.

## Introduction

In binary polymer solvent systems, solvent diffuses due to its own concentration gradient and, one mutual diffusion coefficient describes the transport. The rate of change of solvent concentration at a point equals the gradient of flux there.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left( D(c, T) \frac{\partial c}{\partial z} \right)$$

(1)  $c$  is concentration of the solvent,  $t$  is time,  $z$  is distance and  $D$  is mutual diffusion coefficient, which is a strong function of concentration and temperature,  $T$ . It is predicted accurately for many polymer solvent systems by Vrentas and Duda free volume theory (1977 a, b) in conjunction with Flory-Huggins theory for polymer solution thermodynamics. Many parameters are needed for prediction of the mutual diffusion coefficient; these have been documented by Hong (1995) for several polymers and solvents. In multicomponent systems, a solvent diffuses due to its own concentration gradient and those of other solvents also (Onsager, 1931; DeGroot and Mazur, 1962; Cussler, 1976). Several theories (Zielinski and Hanley (1999), Dabral (1999), Alsoy and Duda (1999), and Price and Romdhane (2003)) for predicting main-term and cross-term diffusion coefficients have appeared in the literature. The theories begin with Bearman's statistical mechanical theory(1961) that relates gradient of chemical potential of a species to frictional motion between the species and others of the system.

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All other previous models (Alsoy and Duda (1999), Zielinski and Hanley (1999) and Dabral (1999)) are some special cases of generalized model (Price and Romdhane, 2003). By setting different values to  $\alpha_i$ , the theories can be recovered. The generalized diffusion equation predicted by them is following

$$D_{11} = c_2 c_3 \hat{V}_2 \left( D_1 \frac{\partial \ln a_1}{\partial c_1} - D_2 \frac{\partial \ln a_2}{\partial c_1} \right) + c_1 c_3 \hat{V}_3 \left( D_1 \frac{\partial \ln a_1}{\partial c_1} - D_3 \frac{\partial \ln a_3}{\partial c_1} \right) \quad (2)$$

$$D_{21} = c_2 c_2 \hat{V}_2 \left( D_1 \frac{\partial \ln a_1}{\partial c_2} - D_2 \frac{\partial \ln a_2}{\partial c_2} \right) + c_1 c_3 \hat{V}_3 \left( D_1 \frac{\partial \ln a_1}{\partial c_2} - D_3 \frac{\partial \ln a_3}{\partial c_2} \right) \quad (3)$$

$$D_{22} = c_2 c_1 \hat{V}_1 \left( D_2 \frac{\partial \ln a_2}{\partial c_1} - D_1 \frac{\partial \ln a_1}{\partial c_1} \right) + c_2 c_3 \hat{V}_3 \left( D_2 \frac{\partial \ln a_2}{\partial c_1} - D_3 \frac{\partial \ln a_3}{\partial c_1} \right) \quad (4)$$

$$D_{23} = c_2 c_1 \hat{V}_1 \left( D_2 \frac{\partial \ln a_2}{\partial c_2} - D_1 \frac{\partial \ln a_1}{\partial c_2} \right) + c_2 c_3 \hat{V}_3 \left( D_2 \frac{\partial \ln a_2}{\partial c_2} - D_3 \frac{\partial \ln a_3}{\partial c_2} \right) \quad (5)$$

The generalized theory requires self-diffusion coefficient of the polymer—a shortcoming of the theory because few experimental data are available for this coefficient. Activity of the solvents for the ternary polymer–solvent–solvent system can be calculated using Flory Huggins theory. Different researchers reported different values for few parameters of free volume. For example, Duda et al., (1982), Vrentas et al., (1985), Vrentas and Chu, (1989) and Alsoy and Duda, (1999) reported different values for  $D_{01}$

and  $\frac{K_{11}}{\gamma}$  for polystyrene – toluene system (Table 1).

Vrentas and Duda (1977) have studied the effect of solvent weight fraction on  $D_{01}$  and results indicates that it value increases by several order of magnitude with increase in solvent weight fraction (Table 2). Vrentas and Chu (1989) studied the effect of polymer molecular weight on  $D_{01}$  and its magnitude increases with decrease in molecular weight

of polymer because of small jumping unit (Table 3). Therefore, it was considered necessary to estimate the free volume parameters for each of the two systems studied. Price et al. (1997) mentioned that out of the nine parameters

$$(D_0, E, \xi, \frac{K_{11}}{\gamma}, K_{21} - T_{gs}, \frac{K_{12}}{\gamma}, K_{22} - T_{gp}, \hat{V}_s^*, \hat{V}_p^*)$$

required to predict mutual diffusion coefficient of a binary

polymer solvent system, five ( $E, \frac{K_{11}}{\gamma}, K_{21} - T_{gs}, \hat{V}_p^*$ , and

$\hat{V}_s^*$ ) can be calculated from the pure substance properties and the remaining four parameters,

$D_0, \xi, \frac{K_{12}}{\gamma}$ , and  $K_{22} - T_{g2}$  can be estimated from

drying experiments. They estimated these four parameters by minimizing the difference between experimental weight loss measurements with predicted ones.

Table 1: Comparison between reported values of free-volume parameters for poly (styrene) – toluene system.

	Duda et al., (1982)	Alsoy and Duda, (1999)	Vrentas and Chu, (1989)	Vrentas et al., (1985)
$D_{01}, \frac{cm^2}{s}$	$615 \times 10^{-4}$	$4.82 \times 10^{-4}$	$4.17 \times 10^{-4}$	$50.3 \times 10^{-4}$
$\frac{K_{11}}{\gamma}$	$22.1 \times 10^{-4}$	$14.5 \times 10^{-4}$	$15.7 \times 10^{-4}$	$15.7 \times 10^{-4}$

Table 2: Effect of solvent weight fraction on  $D_{01}$  for poly (styrene) –ethylbenzene (Vrentas and Duda, 1977).

Mass fraction of Solvent	$D_{01}, \frac{cm^2}{s}$
0	$5.59 \times 10^{-13}$
0.1	$4.38 \times 10^{-7}$
0.2	$9.25 \times 10^{-6}$
0.3	$3.56 \times 10^{-5}$
0.4	$7.62 \times 10^{-5}$
0.5	$1.24 \times 10^{-4}$
0.6	$1.75 \times 10^{-4}$
0.7	$2.26 \times 10^{-4}$
0.8	$2.74 \times 10^{-4}$
0.9	$3.21 \times 10^{-4}$
1	$3.64 \times 10^{-4}$

Table 3: Effect of polymer molecular weight on  $D_{01}$  for toluene- poly (styrene) system (Vrentas and Chu, 1989).

Molecular weight	$D_{01}, \frac{cm^2}{s}$
17400	$1.44 \times 10^{-6}$
110000	$4.42 \times 10^{-7}$
900000	$1.34 \times 10^{-7}$

## Materials and Methods

In the present study, ternary systems consisting of one polymer and two solvents have been considered. The systems chosen for the study were: poly (styrene)-tetrahydrofuran-*p*-xylene and poly (methyl methacrylate)-tetrahydrofuran – ethylbenzene. Four binary solutions of, poly (styrene)-tetrahydrofuran, poly (styrene) - *p*-xylene, poly (methyl methacrylate-ethylbenzene) and poly (methyl methacrylate)-tetrahydrofuran were prepared. Weight loss studies have been done using electronic balance of the coatings of known thicknesses.

## Results and Discussion

The four free volume parameters were estimated along same lines as Price et al. (1997). A code for drying of binary polymer solvent systems was written and used to generate residual solvent as a function of time. Weight loss data was collected for four polymer-solvent pairs, poly (styrene)-tetrahydrofuran, poly (styrene)-*p*-xylene, poly (methyl methacrylate)-ethylbenzene and poly (methyl methacrylate)- tetrahydrofuran at room temperature and quiescent conditions. The difference between experimental and predicted residual solvent, defined here as an objective function, was minimized by using a built-in optimization code, *lsqnonlin*, of MATLAB. Of the nine free volume parameters required to predict diffusion coefficients of binary systems, four for each of the four pairs studied here were estimated as suggested by the literature. Estimation was done by minimizing the difference between predictions of the model and experimental weight loss data for each binary pair. Figures 1 to 4 show that there is good agreement between experiments and model predictions with the optimized values. These are listed in Table 4 for the four pairs. Several sets of the parameters could minimize the objective function. The aim of optimization was to determine a set of parameters that describe drying accurately and not gain physical insight into the system.

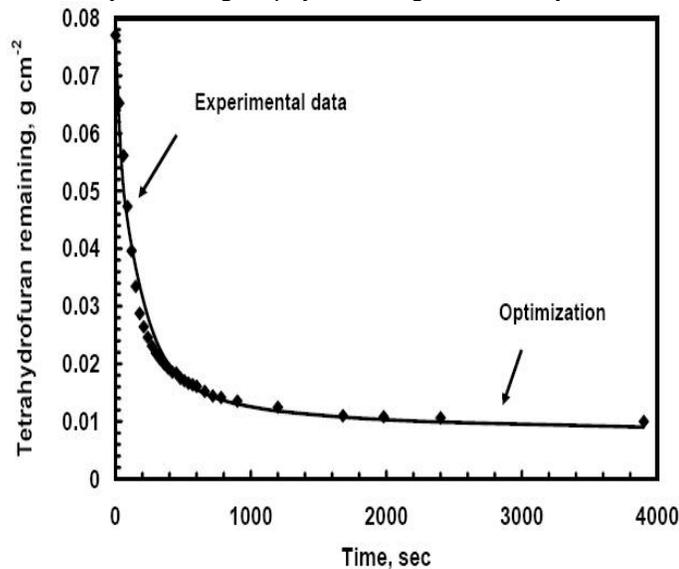


Figure 1: Comparison between experimental and optimized residual solvent for poly (styrene)-tetrahydrofuran system. Initial concentrations of poly (styrene) and tetrahydrofuran were  $0.092$  and  $0.808 \text{ g cm}^{-3}$ , respectively. Air and coating temperatures were  $30^\circ\text{C}$  and coating thickness was  $952$  microns.

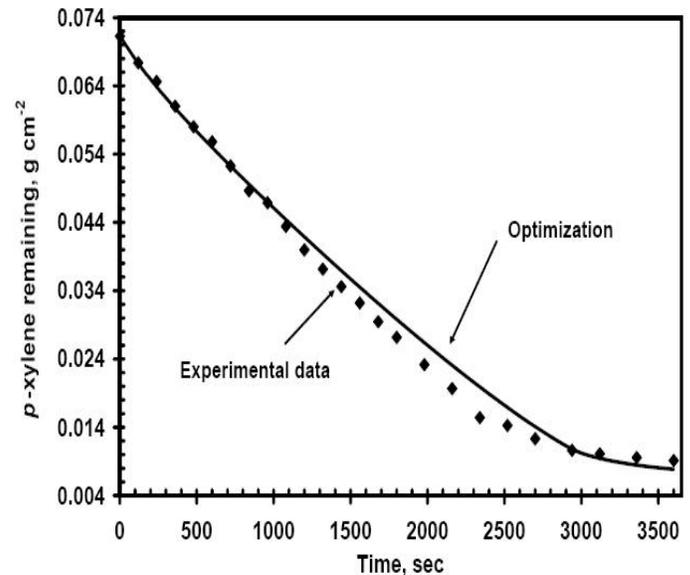


Figure 2: Comparison between experimental and optimized residual solvent for poly (styrene)-*p*-xylene system. Initial concentrations of poly (styrene) and *p*-xylene were  $0.1497$  and  $0.7378 \text{ g cm}^{-3}$ , respectively. Air and coating temperatures were  $29^\circ\text{C}$  and initial coating thickness was  $966$  microns.

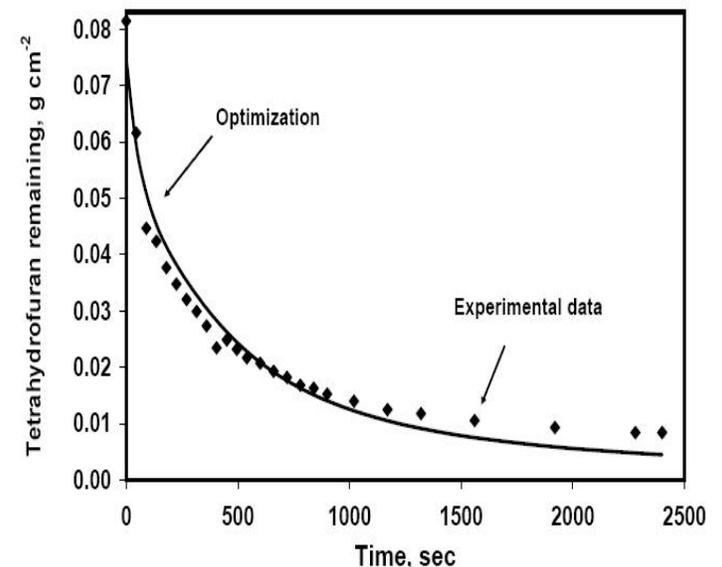


Figure 3: Comparison between experimental and optimized residual solvent for poly (methyl methacrylate) - tetrahydrofuran system. Initial concentrations of poly (methyl methacrylate) and tetrahydrofuran were  $0.1405$  and  $0.7812 \text{ g cm}^{-3}$ , respectively. Air and coating temperatures were  $30^\circ\text{C}$  and initial coating thickness was  $992$  microns.

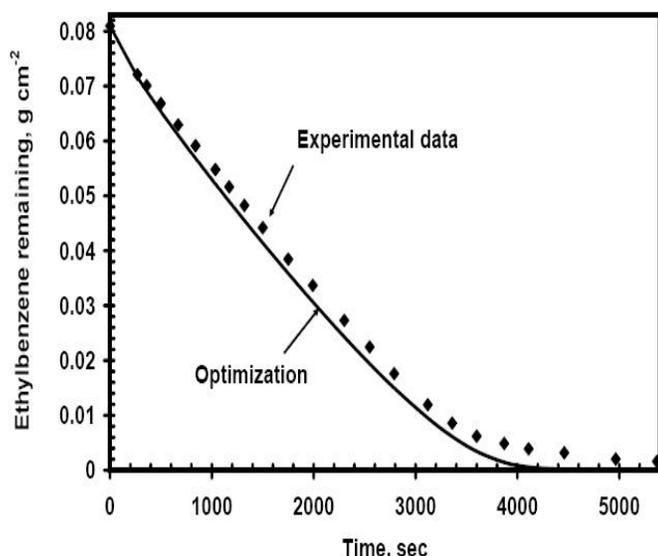


Figure 4: Comparison between experimental and optimized residual solvent for poly (methyl methacrylate) – ethylbenzene system. Initial concentrations of poly (methyl methacrylate) and ethylbenzene were  $0.0809$  and  $0.8069 \text{ g cm}^{-3}$ , respectively. Air and coating temperatures were  $30^\circ\text{C}$  and initial coating thickness was  $1000$  microns.

Table 4: Free volume parameters of four binary polymer solvent systems obtained from optimization.

Parameter	Unit	PS(3)/ THF(2)	PS(3) / <i>p</i> - xylene(1)	PMMA(3)/ THF(2)	PMMA(3)/ EB(1)
$D_0$	$\frac{\text{cm}^2}{\text{s}}$	$97.99 \times 10^{-4}$	$78.44 \times 10^{-4}$	$98.75 \times 10^{-4}$	$4.11 \times 10^{-4}$
$\frac{K_{13}}{\gamma}$	$\frac{\text{cm}^3}{\text{g.K}}$	$2.89 \times 10^{-4}$	$2.89 \times 10^{-4}$	$5.89 \times 10^{-4}$	$5.89 \times 10^{-4}$
$K_{23}$	K	-326.46	-326.46	-230.44	-230.44
$\xi$		0.38	0.44	0.65	0.30

## References

Alsoy, S. and Duda, J. L., 1999, "Modeling of Multicomponent Drying of Polymer Films", *AIChE J.*, 45, 4, 896 – 905.

Bearman, R. J., 1961, "On the Molecular Basis of Some Current Theories of Diffusion", *J. Phys. Chem.*, 65, 1961 - 1968.

Cussler, E. L., 1976, "Multicomponent Diffusion", Elsevier Scientific Pub., Amsterdam, Netherlands.

Dabral, M., 1999, "Solidification of coatings: theory and modeling of drying, curing and microstructure growth", Ph.D. Thesis, Univ. of Minnesota, Minneapolis, MN, USA.

DeGroot, S.R. and Mazur, P., 1962, "Non-Equilibrium Thermodynamics", Amsterdam, North-Holland Pub.

Duda, J. L.; Vrentas, J. S.; Ju, S. T.; Liu, H. T., 1982, "Prediction of Diffusion Coefficients for Polymer-Solvent Systems", *AIChE J.*, 28(2), 279-285.

Hong, S., 1995, "Prediction of Polymer/Solvent Diffusion Behavior Using Free-Volume Theory", *Ind. Eng. Chem. Res.*, 34(7), 2536-2544.

Onsager, L., 1931, "Reciprocal Relations in Irreversible Processes II", *Physical Review*, 38(15), 2265-2279

Price, P. E. Jr. and Romdhane, I. H., 2003, "Multicomponent Diffusion Theory and Its Application to Polymer-Solvent Systems", *AIChE J.*, 49(2), 309 – 322.

Price, P. E. Jr., Wang, S. and Romdhane, I. H., 1997, "Extracting Effective Diffusion Parameters from Drying Experiments", *AIChE J.*, 43(8), 1925-1933.

Vrentas, J. S. and Chu, C. H., 1989, "Molecular-Weight Dependence of the Diffusion Coefficient for the Polystyrene-Toluene System", *J. Poly. Sci., Part B: Poly. Phys.*, 27(2), 465-468.

Vrentas, J. S. and Duda, J. L., 1977a, "Diffusion in Polymer-Solvent Systems. I. Reexamination of the Free-Volume Theory", *J. Poly. Sci.: Poly. Phys. Ed.*, 15, 403-416.

Vrentas, J. S. and Duda, J. L., 1977b, "Diffusion in Polymer – Solvent Systems. II. A Predictive Theory for the Dependence of Diffusion Coefficients on Temperature, Concentration, and Molecular Weight", *J. Poly. Sci.: Poly. Phys. Ed.*, 15, 417-439.

Vrentas, J. S., Duda, J. L., Ling, H. C. and Hou, A. C., 1985, "Free-Volume Theories for Self-Diffusion in Polymer-Solvent Systems. II. Predictive Capabilities", *J. Poly. Sci.: Poly. Phys. Ed.*, 23(2), 289-304.

Zielinski, J. M. and Hanley, B. F., 1999, "Practical Friction-Based Approach to Modeling Multicomponent Diffusion", *AIChE J.*, 45(1), 1 – 12.