

Determination of Thermodynamic and Transport Properties of Solvents and Non Solvents in Poly(L-lactide-co-glycolide)

Hulya Eser, Funda Tihminlioglu

Department of Chemical Engineering, Izmir Institute of Technology, Gülbahçe Urla-İzmir 35430, Turkey

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ABSTRACT: Thermodynamic properties, partition coefficient, and diffusion coefficients of the various solvents (acetone, dichloromethane, trichloromethane, ethyl acetate, ethyl alcohol, tetrahydrofuran, and water) in poly(lactide-co-glycolide) (PLGA) at infinite dilution of the solvent have been determined by inverse gas chromatography (IGC). In IGC method, which is based on the characteristic equilibrium partitioning of a solute between a mobile phase and a stationary phase, a small pulse of solvent is introduced into the column and by the aid of retention volume of the solvent, several polymer solvent interaction properties, namely retention volume (V_g), infinitely dilute weight fraction activity coefficient (Ω_1^∞), Flory–Huggins interaction parameter (χ), and solubility parameters of the polymer (δ_2^∞) can be determined. The thermodynamic results indi-

cated that trichloromethane and dichloromethane were the most suitable solvents among all the solvents studied for PLGA. The partition (K) and diffusion coefficients (D_p) of various solvents at infinite dilution of the solvent were calculated by using the model developed by Pawlisch et al. (Macromolecules 1987, 20, 1564). The optimum K and D_p values that best fit the data were found and the model predicted experimental data very well. So IGC method is a powerful tool for the determination of thermodynamic and diffusion properties of solvent in polymer at infinite dilution of the solvent. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2426–2432, 2006

Key words: inverse gas chromatography; polymer solvent equilibrium; diffusion coefficient; poly(lactide-co-glycolide)

INTRODUCTION

Sorption and diffusion data are pertinent to a variety of applications including membrane separation of gases and vapors, packaging and coating technology, polymer synthesis, controlled drug release systems, and biocompatible materials for biomedical applications.¹

For a polymer solvent system in the presence of very small amounts of solvent, it is difficult to measure the data by using conventional data such as permeation and gravimetric vapor sorption desorption experiments. In the last 20 years, the inverse gas chromatography (IGC) techniques had been developed to measure the solvent diffusion coefficient of polymer solvent at infinite dilution. Packed and capillary chromatographic columns can be used effectively to measure diffusion coefficients.²

Capillary column IGC has been used by many researchers.^{3–5} The principle behind this technique is based on partitioning of a volatile solvent between the mobile gas phase and the stationary polymer phase. Because of the mass transfer resistance in the polymer phase, the material in the mobile phase is swept for-

ward while that in the stationary phase lags behind. The output elution profile of the peak from the gas chromatogram gives the solubility or the partition coefficient and the diffusion coefficient for a polymer solvent system.⁴

The objective of this work was to conduct a detailed study of the thermodynamic and diffusion measurements of poly(lactide-co-glycolide) (PLGA) copolymer with various solvents over a temperature range from 80 to 120°C by IGC. PLGA is a strong candidate as a drug carrier for drug delivery system and can be easily seeded with cells and implanted into the recipient because of its biocompatibility and biodegradability.^{6,7} In recent years, although many studies were reported on the drug release properties of PLGA, to our knowledge, no one reported any thermodynamic and diffusion data for PLGA-solvent systems. Therefore, in this study, an attempt has been done to investigate the diffusion and thermodynamic properties of seven solvents in PLGA at infinite dilution of the solvent.

THEORETICAL

Thermodynamic properties

IGC was used previously by many researchers to study the thermodynamic properties of polymers.^{8,9,10} Only peak retention time data are needed and it is generally expressed as retention volume (V_g^0).

Correspondence to: F. Tihminlioglu (fundatihminlioglu@iyte.edu.tr).

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Specific retention volume at 0°C (V_g^0) was determined experimentally using the following relationship;¹¹

$$V_g^0 = \frac{273.2}{T} \left(\frac{V_N}{w_2} \right) = \frac{273.2}{T w_2} (t_r - t_c) F J \quad (1)$$

where V_N is the net retention volume at temperature in K, w_2 is the mass of polymer, t_r and t_c are the retention times of solute and marker gas, T is the temperature, F is the flow rate of gas, and J is the pressure drop correction factor which is negligible for capillary columns.

The specific retention volume is related to the partition coefficient, K , which is the ratio of concentration of solvent in polymer phase to the concentration of solvent in gas phase, by the following equation;

$$V_g^0 = 273.2 K / T \rho_p \quad (2)$$

where ρ_p is the density of polymer and T is the temperature.

The weight fraction activity coefficient of the solvent at infinite dilution, Ω_1^∞ , was obtained by the following equation;¹²

$$\Omega_1^\infty = \frac{RT}{P_1^\infty V_g^0 M_1} \exp \left(-P_1^s \frac{(B_{11} - V_1)}{RT} \right) \quad (3)$$

where Ω_1^∞ is the infinite dilution activity coefficient, R is the universal gas constant, T is the system temperature, M_1 is the molecular weight of the solute, B_{11} is the second virial coefficient of the solute, V_1 molar volume, and P_1 is the vapor pressure of the solute.

Ω_1^∞ gives an idea of the polymer–solvent compatibility indicating that;

$\Omega_1^\infty < 5$ for good solvents; $5 < \Omega_1^\infty < 10$ for moderate solvents; and $\Omega_1^\infty > 10$ for bad solvents.¹³

The Flory–Huggins interaction parameter (χ_{12}^∞), which was used as a measure of the strength of interaction and therefore as a guide in the prediction of polymer solvent compatibility, is related to the weight fraction activity coefficient by the following equation;¹⁴

$$\chi_{12}^\infty = \ln \Omega_1^\infty - \left(1 - \frac{1}{r} \right) + \ln \frac{\rho_1}{\rho_2} \quad (4)$$

where r is referred to as the number of segments in polymer chain and is given as;

$$r = \frac{\rho_1^* M_2}{\rho_2^* M_1} \quad (5)$$

Here, ρ_i is the density and M_i is the molecular weight of component i .

The values of χ_{12}^∞ greater than 0.5 represent unfavorable polymer–solvent interactions, while the values lower than 0.5 indicate favorable interactions.¹⁵

The solubility parameter for the volatile solvent (δ_1) is generally calculated as follows;

$$\delta_1 = \left[\frac{\Delta H_v - RT}{V_1} \right] \quad (6)$$

where ΔH_v is the heat of vaporization of the solvent. In the calculation of solvent solubility parameter at high temperatures, vapor phase correction is neglected in eq. (6). The effect of high temperature on cohesive energy density [$\Delta H_v/V_1$], and the need to include vapor phase nonideality correction was explained by Huang¹⁶ to estimate the solubility parameter. At temperatures near the critical temperature, the density of the vapor phase gradually increases, and the departure of saturated vapor from the ideal gas becomes significant and needs to be included in the definition of cohesive energy density. At high temperatures, the saturated vapor is in an high temperature and high density state and its internal energy departure from the ideal state, $(E^0 - E)_{\text{vap}}$, should be combined with the heat of vaporization for the calculation of solubility parameter of the solvent, δ_1^* , (with vapor phase nonideality correction).¹⁶ The equation is:

$$\begin{aligned} \delta_1^{*2} &= [\Delta E_{\text{vap}} + (E^0 - E)_{\text{vap}}] / V_{\text{liq}} \\ &= [\Delta H_{\text{vap}} + (H^0 - H)_{\text{vap}} - (RT - PV_{\text{liq}})] / V_{\text{liq}} \quad (7) \end{aligned}$$

The dimensional ratio $(H^0 - H)/T_c$ was correlated for the reduced vapor pressure, $P_{\text{sat},r}$ by;¹⁶

$$\begin{aligned} (H^0 - H)/T_c &= 6.5 P_{\text{sat},r}^{0.62252} / \\ &(1 + 0.76.218(-\ln P_{\text{sat},r})^{0.536042}) \quad (8) \end{aligned}$$

The solubility parameter of the polymer solubility parameter, (δ_2), found by combination of Hildebrand and Flory–Huggins theories is;¹⁷

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi_{12}^\infty}{V_1^0} \right) = \frac{2\delta_2^\infty}{RT} \delta_1 - \left(\frac{\delta_2^\infty}{RT} + \frac{\chi_s}{V_1^0} \right) \quad (9)$$

where δ_1 is the solvent solubility parameter at infinite dilution of the solvent, χ_s is the entropic contribution to χ parameter. After χ_{12}^∞ ($\chi_{12}^\infty = \chi_H + \chi_s$), V_1 and δ_1 are known, the polymer solubility parameter at infinite dilution (δ_2^∞) can be determined graphically by drawing a plot of $(\delta_1^2/(RT) - \chi/V_1)$ versus δ_1 should yield a straight line with $2\delta_2^\infty/(RT)$ as the slope and $-(\delta_2^\infty/(RT) + \chi_s/V_1)$ as the intercept.

Capillary column inverse gas chromatography model

Various mathematical models were developed for both packed and capillary columns.^{5,14} The major

TABLE I
Retention Volumes for PLGA-Solvent Systems

Solutes	V_g (cm ³ /g)			
	80°C	90°C	100°C	120°C
Acetone	19.79	16.07	12.25	7.06
Dichloromethane	19.73	14.69	11.52	7.00
Trichloromethane	34.39	22.33	18.10	10.12
Ethyl acetate	15.15	14.63	12.36	6.90
Ethyl alcohol	17.22	13.51	10.76	4.13
THF	13.52	12.08	10.20	6.88
Water	25.58	18.33	13.47	7.72

disadvantage of the packed column is the difficulty to achieve a uniform polymer film thickness. So, capillary columns are introduced. Pawlisch et al. replaced the packed columns with capillary columns and developed a capillary column inverse gas chromatography model (CCIGC) to measure diffusivities and solubilities. In this study, the model developed by Pawlisch et al. (1985) was used for infinitely dilute region.⁵

They developed the following expression for the concentration profile at the exit of the column in dimensionless Laplace domain;

$$\frac{CL}{C_0u} = \exp\left(\frac{1}{2\Gamma}\right) \exp\left[-\left(\frac{1}{4\Gamma^2} + \frac{s}{\Gamma} + \frac{2\sqrt{s}}{\alpha\beta\Gamma} \tanh \beta\sqrt{s}\right)^{1/2}\right] \quad (10)$$

$$\alpha = \frac{R}{K\tau} \quad \Gamma = \frac{D_g}{uL} \quad \beta^2 = \frac{\tau^2 u}{D_p L} \quad (11)$$

where C is the outlet concentration of the solute in the gas phase, $t_c = L/u$, the residence time of the carrier gas, L is the length of the column, τ is the thickness of the polymer film, s is the Laplace operator, D_g and D_p are gas and stationary phase diffusion coefficients for the solvent respectively, u is the mean velocity of the carrier gas, K is the equilibrium partition coefficient relating gas phase concentration to the polymer phase concentration, α is a thermodynamic parameter whereas Γ and β represent the gas and the polymer phase transport properties.

TABLE II
Weight Fraction Activity Coefficients for PLGA-Solvent Systems

Solutes	Ω_1^∞			
	80°C	90°C	100°C	120°C
Acetone	12.43	11.98	12.52	14.47
Dichloromethane	5.31	5.73	5.98	6.87
Trichloromethane	4.11	4.97	4.89	5.85
Ethyl acetate	20.54	16.12	14.76	16.76
Ethyl alcohol	35.18	31.86	29.15	43.06
THF	19.94	17.40	16.34	16.01
Water	135.46	131.53	127.52	120.36

TABLE III
Interaction Parameters of PLGA-Solvent Systems

Solutes	χ			
	80°C	90°C	100°C	120°C
Acetone	0.98	0.92	0.94	1.05
Dichloromethane	0.64	0.70	0.73	0.82
Trichloromethane	0.52	0.69	0.66	0.81
Ethyl acetate	1.62	1.36	1.25	1.34
Ethyl alcohol	2.04	1.92	1.82	2.18
THF	1.58	1.43	1.35	1.30
Water	3.68	3.64	3.61	3.54

EXPERIMENTAL

Materials

The column prepared by Restek (Bellefonte, PA) was 15 m long with a inner diameter of 0.53 mm and the thickness of the polymer coating was 5 μ m. All solvents, supplied by Aldrich Chemicals were used without further purification which were HPLC grade and were injected as liquids. PLGA was obtained from Aldrich Chemical with a molecular weight of 57,500, density of 1.24 g/cm³, and PLA/GA composition (weight) ratio was 65 : 35, and T_g of 42°C. The temperature dependence of polymer density was neglected.

Experimental set-up

The gas chromatograph used was Shimadzu 17A equipped with a thermal conductivity detector (TCD), a flame ionization detector (FID), an electron capture detector (ECD), a column injector, and an air-circulating oven. Small amounts of solvent were injected through the rubber septum of the injection port into the carrier gas using a Hamilton 1 μ L syringe and air by 10 μ L syringe. The output signal from the detector was stored and recorded in a computer.

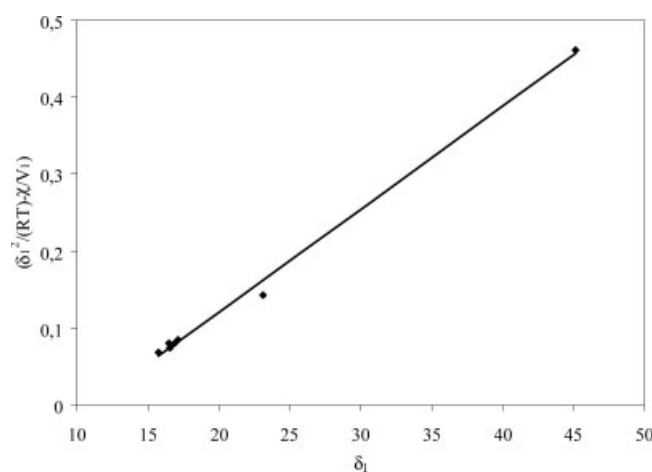


Figure 1 Estimation of PLGA solubility parameter at 373 K.

TABLE IV
Solute Solubility Parameter Data (δ_1)

Solutes	δ_1 (J/cm^3) ^{1/2}			
	80°C	90°C	100°C	120°C
Acetone	17.76	17.35	16.92	15.99
Dichloromethane	18.05	17.58	17.10	16.07
Trichloromethane	17.16	16.81	16.45	15.69
Ethylacetate	16.50	16.14	15.75	14.95
Ethylalcohol	24.06	23.58	23.08	22.01
THF	17.32	16.96	16.59	15.81
Water	45.92	45.53	45.14	44.30

Data analysis

The raw data stored in the computer were converted into ASCII format. Then the data were corrected for baseline offset. After the baseline correction, the elution curve was integrated using a FORTRAN program to determine first and second moments. These moments were used as initial estimates of the partition and diffusion coefficients, K and D_p . The Laplace transform equation was then numerically inverted using an algorithm. The predicted response curve was then compared with the experimental elution curve. The residual was minimized using a nonlinear regression package to find K and D_p that best fit the experimental elution curve. Each experimental point (data) reported in this article is the average of five experimental measurements.

RESULTS AND DISCUSSION

Thermodynamic measurements (retention volume V_g , infinitely dilute weight fraction activity coefficient Ω_1^∞ , polymer solvent interaction parameter χ , solvent and polymer solubility parameters (δ_1 , δ_2), partition coefficients (K), and diffusion coefficients (D_p) of solvents were determined for PLGA–solvent systems by IGC. The measurements were performed at four different temperatures (80, 90, 100, and 120°C) for acetone, dichloromethane, trichloromethane, ethyl acetate, ethyl alcohol, tetrahydrofuran, and water.

TABLE V
Solute Solubility Parameters with Nonideality Correction (δ_1^*)

Solutes	δ_1 (J/cm^3) ^{1/2}			
	80°C	90°C	100°C	120°C
Acetone	18.11	17.78	17.46	16.80
Dichloromethane	18.53	18.17	17.82	17.12
Trichloromethane	17.45	17.17	16.89	16.34
Ethyl acetate	16.71	16.40	16.09	15.47
Ethanol	24.22	23.80	23.37	22.50
THF	17.58	17.29	16.99	16.41
Water	46.00	45.64	45.28	44.53

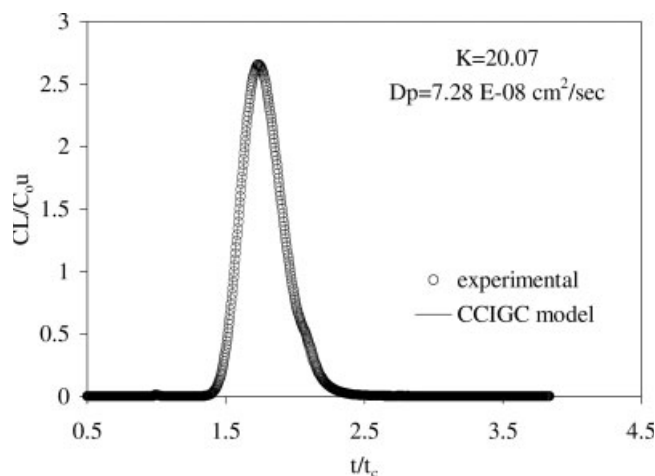


Figure 2 Comparison of experimental and theoretical elution profiles for PLGA ethyl alcohol system at 100°C.

Thermodynamic properties

Retention volume (V_g) of the solvents which is a key parameter and basic step for the determination of thermodynamic properties in polymer–solvent systems by IGC were determined according to eq. (1). The values were tabulated in Table I. As temperature increased retention volume decreased exhibiting the equilibrium sorption occurring in this temperature range. Trichloromethane had the highest value and tetrahydrofuran had the lowest value for all temperatures.

The weight fraction activity coefficient of the solvents which were determined from eq. (3) were listed in Table II. The dependence of activity coefficients on temperature shows different trends for different polymer–solvent systems. Water had the highest value among all the solvents with very high values again showing the poor solvent property for this polymer. Since $\Omega_1^\infty < 5$ for good solvents, trichloromethane was found to be the most suitable solvent for this polymer. Also, dichloromethane had close values to 5 and may be considered a suitable solute for this polymer after trichloromethane. Ω_1^∞ showed weak dependence to temperature except for water which exhibited a decrease in Ω_1^∞ as temperature increased.

Flory–Huggins interaction parameter of seven solvents at four different temperatures (80, 90, 100, and

TABLE VI
Partition Coefficients for PLGA–Solvent Systems

Solutes	80°C	90°C	100°C	120°C
Acetone	38.22	30.12	23.49	15.28
Dichloromethane	33.30	25.73	21.90	13.51
Trichloromethane	53.62	39.95	31.72	20.48
Ethyl acetate	39.37	32.58	25.79	16.45
Ethyl alcohol	32.07	25.41	20.19	12.71
Tetrahydrofuran	35.03	28.98	24.22	16.42
Water	46.46	35.55	28.09	18.04

TABLE VII
Diffusion Coefficients of PLGA-Solvent Systems

Solutes	D_p (cm ² /s)			
	80°C	90°C	100°C	120°C
Acetone	7.01×10^{-9}	2.23×10^{-8}	6.83×10^{-8}	2.57×10^{-7}
Dichloromethane	1.09×10^{-8}	3.08×10^{-8}	9.11×10^{-8}	3.49×10^{-7}
Trichloromethane	6.02×10^{-9}	1.42×10^{-8}	3.72×10^{-8}	1.76×10^{-7}
Ethyl acetate	5.10×10^{-9}	1.39×10^{-8}	3.71×10^{-8}	1.59×10^{-7}
Ethyl alcohol	1.03×10^{-8}	1.39×10^{-8}	7.28×10^{-8}	3.08×10^{-7}
Tetrahydrofuran	4.40×10^{-9}	1.02×10^{-8}	2.78×10^{-8}	1.19×10^{-7}
Water	5.31×10^{-7}	8.43×10^{-7}	1.25×10^{-6}	2.09×10^{-6}

120°C) were determined by using eq. (4) and the values were tabulated in Table III. Since χ_{12} of a solute should be less than 0.5 to be a good solvent for the polymer according to this criteria, it can be expressed as none of the solvents were good solvents for this polymer. But, among them, trichloromethane can be considered as the most suitable one with its close values to 0.5. After trichloromethane, dichloromethane can also be considered a suitable solvent for PLGA. On the other hand, considering all of the solvents studied in this study, water had the highest χ value at all temperatures. This indicated again and confirmed with the other thermodynamic results; water had very poor solubility among the solvents studied for PLGA showing no affinity to this polymer.

A least-square analysis of plots of $(\delta_1^2/(RT) - \chi/V_1)$ versus δ_1 was carried out to obtain the PLGA solubility parameters at 80, 90, 100, and 120°C. These plots give a slope of $2\delta_2^\infty/(RT)$ and an intercept of $-(\delta_2^{\infty 2}/(RT) + \chi V_1)$. Figure 1 shows the solubility parameter calculation of polymer at 100°C without vapor phase correction. Solubility of PLGA at four different temperatures were determined and the values were 21.86, 21.28, 20.78, and 19.77 (J/cm³)^{1/2}, respectively.

The solubility parameters calculated without and with nonideality correction were listed in Tables IV and V, respectively. As can be seen from the tables, the corrected solute solubility parameters were slightly higher than the noncorrected ones. The calculated values of δ_2^{∞} at 80, 90, 100, and 120°C were 22.01, 21.43, 20.93, and 19.93 (J/cm³)^{1/2}, respectively. At these temperatures δ_2^{∞} also showed a linear relationship with temperature. Again, the correction of vapor phase nonideality gave higher solubility parameter for the polymer. Without the correction, the solubility parameters of solvent and polymer tended to be underestimated.¹⁶ Therefore, at high temperatures, vapor phase nonideality should be taken into account for the calculation of the solubility parameter of the solvent.

Solubility parameters are $\delta_1 > 40$ for water, $\delta_1 > 20$ for ethyl alcohol, $\delta_1 < 20$ for acetone, dichloromethane, trichloromethane, ethyl acetate, and THF as indicated in Tables IV and V. If solvent solubility parameters

listed in Tables IV and V were compared with the estimated PLGA solubility parameter, dichloromethane possessed the closest solubility parameters to that of PLGA. Dichloromethane and trichloromethane were the most suitable solvents for PLGA indicating their strong solvency power, just as predicted through the other interaction parameters. Water, on the other hand, with its higher solubility parameters was a poor solvent of PLGA, in agreement with the conclusions based on the other parameters.

The solvents studied in this study were used by many researchers. Liu et al.¹⁸ prepared PLGA microspheres using dichloromethane as the solvent. Tan et al.¹⁹ prepared drug loaded PLGA films for coronary stent applications. Polymer was dissolved in dichloromethane at room temperature to obtain cast film. Karp et al.²⁰ also prepared PLGA films and they dissolved PLGA in trichloroform solution. So, the literature studies supported our results indicating that trichloromethane and dichloromethane are the most suitable solvents for PLGA.

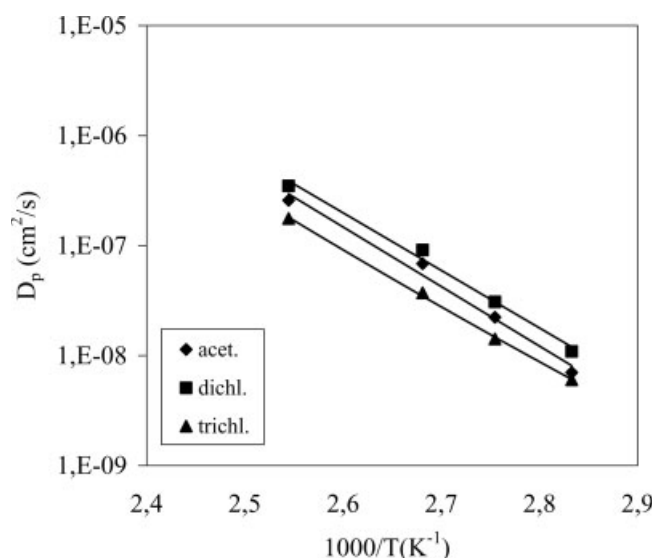


Figure 3 Temperature dependence of D_p for various solvents in PLGA.

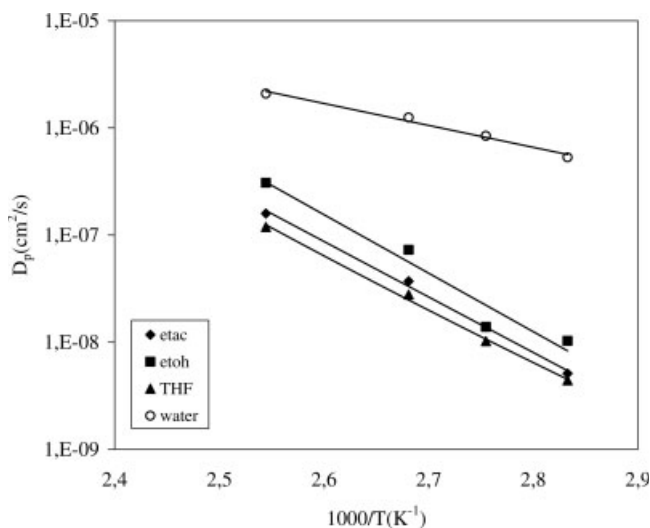


Figure 4 Temperature dependence of D_p for various solvents in PLGA.

Partition and diffusion coefficient measurements of PLGA-solvent systems

The partition and diffusion measurements of acetone, dichloromethane, trichloromethane, ethyl acetate, ethyl alcohol, tetrahydrofuran, and water in PLGA were measured by IGC using TCD over a temperature range of 80–120°C, which was above the glass transition temperature of the polymer ($T_g = 42^\circ\text{C}$).

Figure 2 shows the theoretical and experimental elution profiles of ethyl alcohol at 100°C. The points and solid lines in these figures represent the experimental and theoretical data, respectively. The partition (K) and diffusion coefficients (D_p) were obtained by regressing these curves. These curves exhibited that the model described the data well.

The values of infinitely dilute partition coefficients (K) of acetone, dichloromethane, trichloromethane, ethyl acetate, ethyl alcohol, tetrahydrofuran, and water at 80–120°C were tabulated in Table VI. This table exhibited that partition coefficient increased as temperature decreased indicating that the partition coefficient was inversely related to the temperature of the system. The functionality of $\log(K)$ with temperature was linear for all the solvents studied at temperatures higher than the glass transition of the polymer as expected and found by other researchers.^{3,5,21} An error analysis on K values was also performed. When standard deviation was calculated, it was found in the range of 0.02–0.69.

The infinitely dilute diffusion coefficients (D_p) of acetone, dichloromethane, trichloromethane, ethyl acetate, ethyl alcohol, tetrahydrofuran, and water at 80, 90, 100, and 120°C were tabulated in Table VII. Water had the highest diffusion coefficient values (5.3×10^{-7} – 2.1×10^{-6} cm²/s) at all temperatures and tetrahydrofuran had the lowest D_p values (4.4×10^{-9} – 1.2×10^{-7} cm²/s). The temperature dependence

of D_p were plotted for these solvents and shown in Figures 3 and 4. Figures 3 and 4 indicate that the D_p increases with temperature. That behavior follows Arrhenius relationship.

CONCLUSIONS

Polymer–solvent interactions, partition, and diffusion coefficients at infinite dilution of solvent were obtained for various solvents in PLGA by IGC. Since IGC technique is rapid, simple, and reliable; this technique has been preferred by many authors to obtain polymer–solvent interactions. In this study, both thermodynamic and diffusion measurements were performed by this technique.

Thermodynamic results obtained in this study were used to reveal useful information about the degree of compatibility between PLGA and the various solvents used. The weight fraction activity coefficient Ω_1^∞ , Flory–Huggins interaction parameters χ of various solvents in PLGA were determined, and trichloromethane and dichloromethane were obtained as the most suitable solvents for PLGA. Water showed no affinity for this polymer with its high Ω_1^∞ and χ values. The solubility parameters of both solvents (δ_1) and polymer (δ_2) were also estimated. The prediction of the degree of compatibility of the various solvents with PLGA using the solubility concept agreed well with that obtained through the stability analysis approach by using χ parameter.

The mathematical model derived by Pawlisch et al. (1987) for calculating the partition and diffusion coefficients of solvents in polymers at infinite dilution of solvent was used. The optimum K and D_p values that best fit the data were well found and the model predicted the experimental data well. The effect of temperature on partition and diffusion coefficients was investigated, and it was observed that as temperature increased partition coefficient decreased whereas diffusion coefficient increased.

NOMENCLATURE

C	solute concentration in the gas phase [mol/cm]
C'	solute concentration in polymer phase [mol/cm]
D_g	solvent diffusion coefficient in the mobile phase [cm ² /s]
D_p	solvent diffusion coefficient in the polymer phase [cm ² /s]
K	equilibrium partition coefficient
M_i	molecular weight of the component i [g/mol]
R	gas constant [J/mol K]
r	radial direction [cm]
S	Laplace operator
t	time [s]

T	temperature [K]
T_{gi}	glass transition temperature of component i [K]
u	mean velocity of the carrier gas [cm/s]
z	axial direction

Greek letters

α	nondimensional thermodynamic parameter
β	nondimensional polymer phase diffusion parameter
Γ	nondimensional gas phase diffusion parameter
τ	film thickness in the capillary column [cm]
χ	Flory-Huggins polymer-solvent interaction parameter
Ω_i	weight fraction of component i
δ_i	solubility parameter [J/cm^3] ^{1/2}

References

- Rodriguez, O.; Fornasiero, F.; Arce, A.; Radke, C. J.; Praustnitz, J. M. *Polymer* 2003, 44, 6323.
- Jiang, W. H.; Liu, H.; Hu, H. J.; Han, S. J. *Eur Polym J* 2001, 37, 1705.
- Tihminlioglu, F.; Surana, R. K.; Danner, R. P.; Duda, J. L. *J Polym Sci Part B: Polym Phys* 1997, 35, 1279.
- Surana, R. K.; Danner, R. P.; Tihminlioglu, F.; Duda, J. L. *J Polym Sci Part B: Polym Phys* 1997, 35, 1233.
- Pawlisch, C. A.; Macris, A.; Laurence, R. L. *Macromolecules* 1987, 20, 1564.
- Mercier, N. R.; Costantino, H. R.; Tracy, M. A.; Lawrescence, J. B. *Biomaterials* 2005, 26, 1945.
- Kim, D.; El-shall, H.; Dennis, D.; Morey, T. *Colloids Surf B* 2005, 40, 83.
- Zhao, L.; Choi, P. *Polymer* 2001, 42, 1075.
- Kaya, İ.; Özdemir, E. *Polymer* 2001, 42, 2405.
- Tyagi, O. S.; Deshpande, D. D. *Polym J* 1987, 19, 1231.
- Laub, R. L.; Pecsok, R. L. *Physicochemical Applications of Gas Chromatography*; Wiley: New York, 1978.
- Braun, J. M.; Guillet, J. E. *Adv Polym Sci* 1976, 21, 107.
- Guillet, J. E.; Purnel, J. H. *Advances in Analytical Chemistry and Instrumentation, Gas Chromatography*; Wiley: New York, 1973.
- Gray, D. G.; Guillet, J. E. *Macromolecules* 1973, 6, 223.
- Demirelli, K.; Kaya, İ.; Coşkun, M. *Polymer* 2001, 42, 5181.
- Huang, J. C. *J Appl Polym Sci* 2004, 94, 1547.
- Romdhane, I. H. M.S. Thesis, Pennsylvania State University, University Park, PA, 1990.
- Liu, F. I.; Kuo, J. H.; Sung, K. C.; Hu, O. Y. P. *Int J Pharm* 2003, 257, 23.
- Tan, L. P.; Venkatraman, S. S.; Sung, P. F.; Wang, X. T. *Int J Pharm* 2004, 283, 89.
- Karp, J. M.; Shoichet, M.; Davies, J. E. *J Biomed Mater Res A* 2003, 64, 388.
- Romdhane, I. H.; Danner, R. P.; Duda, J. L. *Ind Eng Chem Res* 1995, 34, 2833.