

Solubility and diffusivity of solvents and nonsolvents in poly(methyl methacrylate co butyl methacrylate)

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Abstract

In this study, thermodynamic properties, namely retention volume, infinitely dilute weight fraction activity coefficient, Flory–Huggins interaction parameter, solubility parameter of the polymer, partition coefficient and diffusion coefficients of the various solvents in poly(methyl methacrylate co butyl methacrylate) (PMMA co BMA) at infinite dilution of the solvent have been determined by inverse gas chromatography (IGC). In this technique, a small amount of the solvent was injected into the capillary column and its retention time was measured and used to calculate several polymer–solvent interaction parameters which are mentioned above. The solvents used in this study were methanol, ethanol, propanol, butanol, methyl acetate, ethyl acetate, propyl acetate, dichloromethane, trichloromethane, acetone, methyl methacrylate, butyl methacrylate for PMMA co BMA. The thermodynamic results, obtained from the experiments, indicated that trichloromethane and dichloromethane were the most suitable solvents among all the solvents studied for PMMA co BMA. 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. [C.A. Pawlisch, A. Macris, R.L. Laurence, Solute diffusion in polymers. I. The use of capillary column inverse gas chromatography, *Macromolecules* 20 (1987) 1564–1578]. The optimum K and D_p values that best fit the data were found and the model predicted experimental data very well. Vrentas–Duda free volume theory was used to correlate the diffusion data and to investigate the effect of solvent size on diffusion process. The theory has shown to correlate diffusion data above the glass transition temperature very well for the PMMA-co-BMA–solvent system.

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1. Introduction

Molecular diffusion of solutes and monomers is important and finds wide range of applications in many areas including solvent devolatilization, residual monomers stripping, packaging, polymer synthesis, drying of paints and coating processes. In these processes it is necessary to know transport and thermodynamic data of the polymer–solvent system. Various techniques exist to measure these data including gravimetric sorption, piezoelectric sorption, nuclear magnetic resonance, light scattering and inverse gas chromatography (IGC) [1,2]. Conventional methods like gravimetric sorption rely on bulk equilibration and hence it is slow. Despite this, inverse gas chromatography is a fast, reliable, accurate, simple and commonly used technique to measure the diffusion coefficients as small as 10^{-13} cm²/s,

applicable at both above and below the glass transition temperature of the polymer [1–3].

Capillary column inverse gas chromatography has been used by many researchers [2,4,5]. The principle behind this technique is based on partitioning of a volatile solvent between the mobile gas phase and the stationary polymer phase. Due to the mass transfer resistance in the polymer phase, the material in the mobile phase is swept forward 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].

Free volume theory which was used to correlate and predict the diffusion coefficients, was developed by Vrentas and Duda [6] to investigate the diffusion behavior in polymeric materials. This method correlates and predicts the diffusion in a polymer–solvent system and was based on free volume model developed by Cohen and Turnbull [7]. Vrentas and Duda extended this theory to binary polymer–solvent systems and derived expressions for the concentration and temperature

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dependence of the solvent diffusion coefficient in a polymer solution [6].

The objective of this work was to conduct a detailed study of the thermodynamic and diffusion measurements of poly(methyl methacrylate co butyl methacrylate) (PMMA co BMA) copolymer with various solvents over a temperature range from 150 to 200 °C by IGC. In recent years, water based polymer latexes which have gained more attention in the coating and adhesives industries over conventional solvent based systems. Production of particles of methymethacrylate-butylmethacrylate copolymers could be produced by microemulsion polymerization [8–10]. Despite the industrial importance of the microemulsion polymerization of MMA–BMA copolymers, to our knowledge no one has reported any thermodynamic and diffusion data for PMMA co-BMA/solvent systems. Therefore, in this study, attempt has been made to investigate the diffusion and thermodynamic properties of twelve solvents in PMMA-co-BMA at infinite dilution of the solvent. Vrentas–Duda free volume theory was used to correlate the experimental diffusion data at different temperatures.

2. Theoretical

2.1. Thermodynamic properties

Inverse gas chromatography was used previously by many researchers to study the thermodynamic properties of polymers [3,11,12]. The parameter most often measured by this technique is the specific retention volume at 0 °C (V_g^0), defined as [13],

$$V_g^0 = \frac{273.2}{T} \left(\frac{V_N}{w_2} \right) = \frac{273.2}{Tw_2} (t_r - t_c) FJ \quad (1)$$

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, 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:

$$V_g^0 = \frac{273.2K}{T\rho_p} \quad (2)$$

where ρ_p is the density of the polymer.

The retention volume data can be determined by using two methods: (1) from the time of the peak maximum and (2) from the first moment of the peak. It has been shown that both methods have been useful in obtaining thermodynamic and transport information in polymer–solvent systems by Davis et al. [14]. They concluded that retention volume diagram (the natural logarithm of retention volume versus reciprocal temperature) should be linear if first moment is used to calculate the retention volume. Unless surface adsorption makes a contribution to first moment, the retention diagram based on first moment will be linear [14].

The weight fraction activity coefficient of the solvent at infinite dilution, Ω_1^∞ , was obtained by the following equation [15]:

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

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; $\Omega_1^\infty < 5$ good solvents; $5 < \Omega_1^\infty < 10$ moderate solvents; $\Omega_1^\infty > 10$ bad solvents [16].

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 [17]:

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

where r is referred to as number of segments in polymer chain and 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 [18]

The solubility parameter for the volatile solvent (δ_1) is found as follows:

$$\delta_1 = \left[\frac{\Delta H_v - RT}{V_1} \right]^{1/2} \quad (6)$$

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 non ideality correction was explained by Huang et al. [19] 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 ($E^o - E$)_{vap}, should be combined with the heat of vaporization for the calculation of solubility parameter of the solvent, δ_1^* (with vapor phase non ideality correction) [19]. The equation is;

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

The dimensional ratio $(H^o - H)/T_c$ was correlated for the reduced vapor pressure, $P_{\text{sat},r}$, by [19];

$$\frac{(H^o - H)}{T_c} = \frac{6.5 P_{\text{sat},r}^{0.62252}}{(1 + 0.76.218(-\ln P_{\text{sat},r})^{0.536042})} \quad (8)$$

Then, the solubility parameter of the polymer (δ_2), is found by combination of Hildebrand and Flory–Huggins Theories is [20]

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

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 $-(\delta_2^{\infty 2}(RT) + \chi_S/V_1)$ as the intercept.

2.2. Capillary column inverse gas chromatography model

Various mathematical models were developed for both packed and capillary columns [5,17]. The major 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. 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;

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

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

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, K is the equilibrium partition coefficient relating gas phase concentration to the polymer phase concentration, α is a thermodynamic parameter where as Γ and β represent the gas and the polymer phase transport properties.

2.3. Free volume theory

Free volume concepts were used to describe the diffusion of low molecular weight penetrants or solvents in amorphous polymer. These concepts were first introduced by Cohen and Turnbull

[7] and modified by Fujita [21] for diffusivities in amorphous polymers and rubbers and redefined by Vrentas and Duda for self and mutual diffusion coefficients of solvents in polymers. Vrentas and Duda [6] derived the following expression for the concentration and temperature dependence of solvent self diffusion in a polymer solution above T_g ;

$$D_1 = D_{01} \exp\left(\frac{-\gamma(w_1 \hat{V}_1^* + w_2 \hat{V}_2^* \varepsilon)}{\hat{V}_{FH}}\right) \quad (12)$$

here w_i is the weight fraction, D_{01} is the preexponential factor, γ is the overlap factor, \hat{V}_i^* is the specific hole free volume of component i required for a diffusive jump, \hat{V}_{FH} is the specific hole free volume and quantity ε is defined as follows:

$$\varepsilon = \frac{M_{j1} \hat{V}_1^*}{M_{j2} \hat{V}_2^*} \quad (13)$$

where M_{ji} is the molecular weight of a jumping unit of component i .

Vrentas and Duda developed a relationship between the hole free volume and well defined volumetric characteristics of the pure components in solution:

$$\hat{V}_{FH} = w_1 K_{11}(K_{21} - T_{g1} + T) + w_2 K_{12}(K_{22} - T_{g2} + T) \quad (14)$$

where K_{11} and K_{21} denote free volume parameters for the solvent, while K_{12} and K_{22} are free volume parameters for the polymer. The glass transition temperature of species are given by T_{gi} .

Eq. (12) can be used to regress experimental data for D_{01} and ε . Once these parameters are known, free volume can then be used to interpolate and extrapolate the diffusion coefficients over a wide ranges of temperatures and concentrations.

3. Experimental

3.1. Materials

The capillary column was prepared by the Restek Co. (Bellefonte, PA). The column was 15 m long with a inner diameter of 0.53 mm and the thickness of the polymer coating of 6 μm . All solvents, supplied by Aldrich Chemicals were used without further purification and were injected as liquids. Random PMMA co BMA was obtained from Aldrich Chemical with a molecular weight of 75,000 and PMMA/BMA composition (weight) ratio was 85:15 and a T_g of 105 °C and a density value of 1.115.

3.2. Experimental set-up

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

3.3. 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. This analysis is derived for an infinitely dilute concentration of solvent in the polymer and this method was used by many authors [2,4,22]. Each experimental point (data) reported in this article is the average of five experimental measurements.

4. Results and discussion

Both thermodynamic (retention volume V_g^0 , infinitely dilute activity coefficient Ω_1^∞ , polymer solvent interaction parameter χ , polymer solubility parameter, δ_2 , and transport properties (diffusion coefficient D_p , partition coefficient K) of 12 solvents in PMMA co BMA were determined by inverse gas chromatography from 150 to 200 °C.

4.1. Thermodynamic properties

Retention volume (V_g^0) is a key parameter to obtain the thermodynamic properties of the system by inverse gas chromatography. V_g of the solvents for the polymethyl methacrylate co butyl methacrylate at four different temperatures were determined using Eq. (1) using the peak maximum method and reported in Table 1. V_g of the solvents were also found by using the first moment of the elution peaks. The retention diagram based on the peak maximum and the first moment was linear. Both methods gave a similar result with a less than 5% error for all the solvents studied. Fig. 1 shows an example of a retention diagram of dichloromethane-PMMA-co BMA system. Gener-

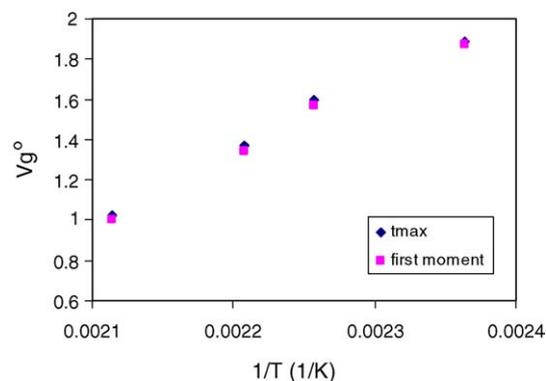


Fig. 1. Example of a retention diagram for dichloromethane-PMMA-co BMA system above T_g .

ally V_g decreased linearly as temperature increased. This linear behavior showed that the peak maximum is equivalent to the first moment at temperature range studied which was above T_g .

The weight fraction activity coefficients (Ω_1^∞) of the solvents in PMMA co BMA were determined by using Eq. (3) and tabulated in Table 2. Activity results showed that, among the solvents studied, trichloromethane had the lowest activity coefficient at the same temperature and methanol had the greatest value in a significant manner. According to our findings based on the 12 solvents studied in this polymer, we can say that trichloromethane is the best solvent for this polymer. Although Ω_1^∞ exhibited a maximum at 200 °C, it was found that Ω_1^∞ was not a strong function of temperature.

Flory–Huggins interaction parameter values (χ) for 12 solvents with PMMA co BMA were calculated by using Eq. (4) at four different temperatures (150, 170, 180, 200 °C). A close inspection of the tabulated interaction data revealed useful information about the degree of compatibility between PMMA co BMA and the various solvents used in this study. When the stability analysis was applied to the Flory–Huggins equation, complete polymer solubility exists only when χ is less than 0.5 [18]. If the χ parameters in Table 3 were examined, trichloromethane appeared to have the minimum value for χ at all temperatures except 150 °C at which dichloromethane had the lowest value. Thus, one may predict that trichloromethane is the most suitable

Table 1
Retention volumes for PMMA co BMA-solvent systems

Solutes	V_g^0			
	150 °C	170 °C	180 °C	200 °C
Methanol	4.25	3.03	2.69	1.61
Ethanol	5.22	3.86	3.35	2.08
1-Propanol	7.72	6.29	5.55	3.36
1-Butanol	12.03	10.08	7.37	5.25
Methyl acetate	4.12	3.57	2.97	1.99
Ethyl acetate	4.93	4.42	3.87	2.39
Propyl acetate	6.85	6.12	5.64	3.82
Dichloromethane	6.60	4.95	3.94	2.79
Trichloromethane (chloroform)	7.58	7.58	6.25	4.30
Acetone	4.50	3.65	3.10	2.19
MMA	7.76	7.23	6.33	4.36
BMA	21.35	20.52	16.84	11.10

Table 2
Weight fraction activity coefficients for PMMA co BMA-solvent systems

Solutes	Ω_1^∞			
	150 °C	170 °C	180 °C	200 °C
Methanol	88.31	83.09	77.89	92.54
Ethanol	16.88	15.56	15.18	18.29
1-Propanol	10.21	8.64	8.33	10.48
1-Butanol	11.20	8.75	9.93	10.03
Methyl acetate	11.73	10.27	10.93	13.15
Ethyl acetate	13.34	10.92	10.86	13.78
Propyl acetate	16.79	10.51	10.86	12.07
Dichloromethane	4.66	4.86	5.46	6.37
Trichloromethane	4.70	3.74	3.78	4.37
Acetone	13.70	12.80	13.34	15.32
MMA	14.18	10.82	10.60	11.59
BMA	16.98	10.86	10.61	10.80

Table 3
Interaction parameters of PMMA co BMA-solvent systems

Solutes	χ_{12}			
	150 °C	170 °C	180 °C	200 °C
Methanol	3.00	2.88	2.79	2.89
Ethanol	1.29	1.16	1.10	1.22
1-Propanol	0.76	0.54	0.47	0.62
1-Butanol	0.92	0.64	0.74	0.71
Methyl acetate	1.05	0.85	0.88	0.98
Ethyl acetate	1.16	0.91	0.87	1.04
Propyl acetate	1.40	0.89	0.90	0.95
Dichloromethane	0.47	0.45	0.54	0.60
Trichloromethane	0.64	0.36	0.35	0.44
Acetone	1.03	0.90	0.90	0.95
MMA	1.30	0.99	0.95	0.99
BMA	1.47	0.99	0.95	0.94

solvent for PMMA co BMA. On the other hand, considering all of the solvents studied in this study, methanol had the highest χ value at all temperatures. This indicated that methanol had very poor solubility characteristic among the studied solvents for PMMA co BMA showing no affinity to this polymer as manifested by their relatively high χ values and the decreasing values of Ω_1^∞ with increasing temperature. Previously the highest Ω_1^∞ values also proved that methanol was the unsuitable solvent for PMMA co BMA. In the alcohol series, propanol has the minimum value but still all of its values at these temperatures are higher than 0.5. The monomers of PMMA co BMA gave similar interaction parameters and the values were higher than 0.5 at all temperatures.

A least-square analysis of plots of $(\delta_1^2/(RT) - \chi_{12}/V_1)$ versus δ_1 was carried out to obtain the PMMA co BMA solubility parameters at 150, 170, 180, 200 °C. These plots give a slope of $2\delta_2^\infty(RT)$ and an intercept of $-(\delta_2^{\infty 2}(RT) + \chi V_1)$. Fig. 2 shows the solubility parameter calculation of polymer at 200 °C without vapor phase correction. Derived values of δ_2^∞ at 150, 170, 180, 200 °C were 15.22, 13.81, 13.37, and 11.79 (J/cm³)^{1/2}, respectively. The temperature dependence of the solubility parameter obtained for PMMA co BMA is shown in Fig. 3 with a linear correlation coefficient greater than 0.993. The solvent solubility parameters calculated without and with nonideality correction were listed in Tables 4 and 5, respectively.

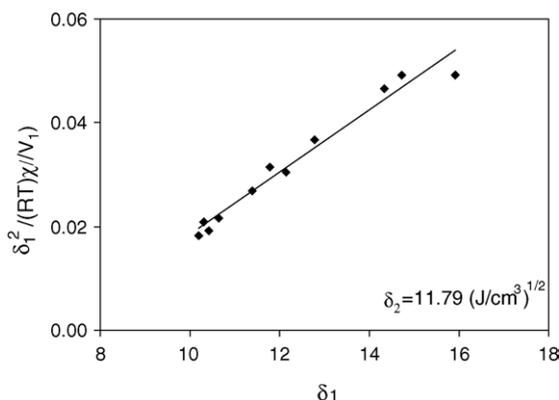


Fig. 2. Estimation of PMMA co BMA solubility parameter at 200 °C.

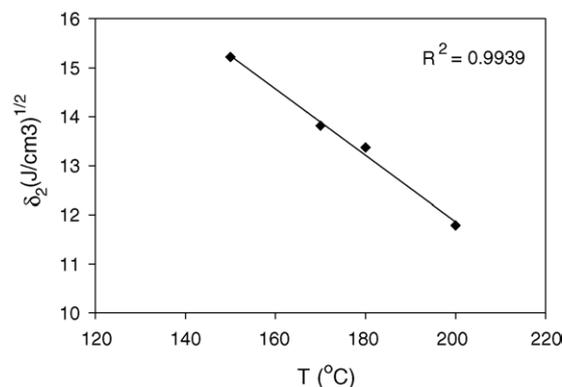


Fig. 3. Solubility parameter of PMMA co BMA as a function of temperature.

Table 4
Solute solubility parameter data (δ_1)

Solutes	δ_1 (J/cm ³) ^{1/2}			
	150 °C	170 °C	180 °C	200 °C
Methanol	21.97	20.22	19.22	16.83
Ethanol	20.17	18.72	17.90	15.92
1-Propanol	18.07	16.75	16.01	14.33
1-Butanol	17.69	16.59	16.00	14.71
Methyl acetate	13.93	12.67	11.95	10.19
Ethyl acetate	13.60	12.56	11.98	10.65
Propyl acetate	13.72	12.87	12.41	11.39
Dichloromethane	14.31	12.94	12.16	10.29
Trichloromethane	14.43	13.48	12.95	11.78
Acetone	14.37	13.05	12.29	10.42
MMA	14.39	13.55	13.10	12.13
BMA	14.24	13.68	13.39	12.77

It can be seen that, the corrected solute solubility parameters were slightly higher than noncorrected ones. The calculated values of $\delta_2^{*\infty}$ at 150, 170, 180, 200 °C were 16.00, 15.10, 14.88, and 13.76 (J/cm³)^{1/2}, respectively. At these temperatures $\delta_2^{*\infty}$ also showed a linear relationship with temperature. Again, the correction of vapor phase non ideality gave higher solubility parameter for the polymer. Without the correction, the solubility parameters of solvent and polymer tended to be underestimated

Table 5
Solute solubility parameters with correction (δ_1^a)

Solutes	δ_1 (J/cm ³) ^{1/2}			
	150 °C	170 °C	180 °C	200 °C
Methanol	22.36	20.78	19.90	17.82
Ethanol	21.16	20.23	19.75	18.70
1-Propanol	18.96	18.11	17.68	16.81
1-Butanol	18.17	17.34	16.92	16.08
Methyl acetate	15.32	14.66	14.31	13.57
Ethyl acetate	14.53	13.91	13.59	12.93
Propyl acetate	14.29	13.70	13.40	12.80
Dichloromethane	16.10	15.43	15.10	14.41
Trichloromethane	15.54	15.03	14.78	14.29
Acetone	15.79	15.08	14.71	13.88
MMA	14.93	14.31	14.01	13.40
BMA	14.40	13.92	13.68	13.21

^a With vapor phase non ideality correction.

[19]. Therefore, at high temperatures, vapor phase non ideality should be taken into account for the calculation of the solubility parameter of the solvent.

By comparing the solvent solubility parameters, δ_1 , listed in Tables 4 and 5 with the estimated PMMA co BMA solubility parameter, one could distinguish between solvents and non solvents. Good examples were dichloromethane and trichloromethane which possessed the closest solubility parameters to that of PMMA co BMA, indicating their strong solvency power, just as predicted through the other interaction parameters. Alcohols, especially methanol, on the other hand, with their higher solubility parameters were poor solvents of PMMA co BMA, in agreement with the conclusions based on the other parameters.

In general, the prediction of the degree of compatibility of the various solvents with PMMA co BMA using the solubility concept agreed well with that obtained through the stability analysis approach by using χ_{12} parameter.

4.2. Diffusion measurements of PMMA co BMA-solvent systems

The partition and diffusion measurements of twelve solvents were performed in PMMA co BMA over a temperature range of 150–200 °C, which was well above the glass transition temperature of the polymer ($T_g = 105$ °C). The diffusion and partition coefficients of methanol, ethanol, propanol, butanol, methyl acetate, ethyl acetate, propyl acetate, dichloromethane, trichloromethane, acetone, methyl methacrylate, butyl methacrylate at 150, 170, 180, 200 °C were determined by flame ionization detector.

Fig. 4 shows the theoretical and experimental elution profiles of methanol at 170 °C. The points and solid lines in this figure represent the experimental and theoretical data, respectively. The partition (K) and diffusion coefficients (D_p) were obtained by regressing these curves. The good agreement between experimental and CCIGC model accurately describes the chromatographic process.

The values of infinitely dilute partition coefficients (K) of methanol, ethanol, propanol, butanol, methyl acetate, ethyl

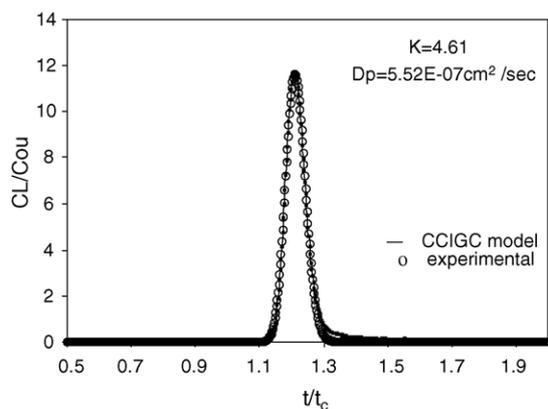


Fig. 4. Comparison of experimental and theoretical elution profiles for PMMA co BMA-methanol system at 443 °K.

Table 6
Partition coefficients for solvent-PMMA co BMA system

Solutes	K			
	150 °C	170 °C	180 °C	200 °C
Methanol	6.34	4.60	3.96	2.96
Ethanol	8.47	6.12	5.10	3.89
1-Propanol	14.41	10.34	8.78	6.31
1-Butanol	24.38	16.73	13.97	9.89
Methyl acetate	7.74	5.66	4.17	3.68
Ethyl acetate	10.40	7.56	6.40	4.79
Propyl acetate	15.70	11.49	9.43	7.24
Dichloromethane	10.55	7.78	6.47	5.07
Chloroform	15.75	12.93	10.20	7.96
Acetone	7.90	6.08	5.01	3.89
MMA	17.94	12.68	10.73	7.87
BMA	50.97	35.44	28.82	19.76

acetate, propyl acetate, dichloromethane, trichloromethane, acetone, methyl methacrylate, butyl methacrylate at 150, 170, 180, 200 °C at infinite dilution were tabulated in Table 6. Table 6 exhibited that partition coefficient increased as temperature decreased indicating that the solvent solubility was inversely related to the temperature of the system. The change in partition coefficient was greater at lower temperatures. An error analysis on K values was also performed. When standard deviation were calculated, it was in the range of 0.06–0.4. For PMMA co BMA/methyl acetate system, the change of partition coefficient with temperature was shown in Fig. 5. This figure exhibited that the results were reproducible.

Clearly, the functionality of $\log(K)$ with temperature is linear for all solvents studied at temperatures above the glass transition of the polymer as expected and found by other researchers [2,5,23]. For the alcohols butanol had the highest partition coefficient and methanol had the lowest partition coefficient since the molecular weight of butanol was greater than methanol. Acetates reflected the same behavior for the molecular weight dependence of partition coefficient propyl acetate had the highest K value at all temperatures among the acetates supporting this idea.

Among the partition coefficients for dichloromethane, trichloromethane and acetone, trichloromethane had the greatest value and acetone had the lowest at all temperatures. This demonstrates that PMMA co BMA was more soluble in trichloromethane than dichloromethane and acetone.

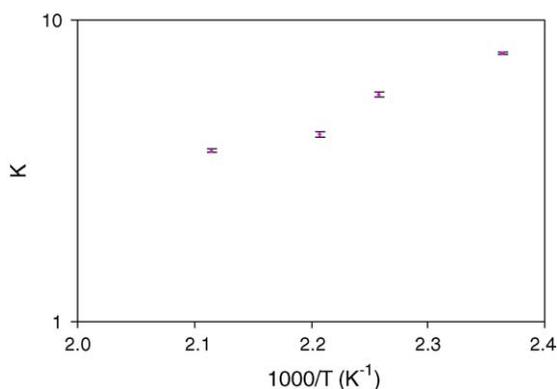


Fig. 5. Error analysis for methyl acetate-PMMA co BMA system.

Table 7
Diffusion coefficients for solvent-PMMA co BMA system

Solutes	D_p (cm ² /s)			
	150 °C	170 °C	180 °C	200 °C
Methanol	2.20×10^{-7}	5.64×10^{-7}	8.05×10^{-7}	1.38×10^{-6}
Ethanol	4.36×10^{-8}	1.34×10^{-7}	2.08×10^{-7}	4.91×10^{-7}
1-Propanol	1.48×10^{-8}	5.25×10^{-8}	8.62×10^{-8}	2.41×10^{-7}
1-Butanol	8.20×10^{-9}	3.38×10^{-8}	6.24×10^{-8}	1.94×10^{-7}
Methyl acetate	2.54×10^{-8}	8.48×10^{-8}	1.39×10^{-7}	3.41×10^{-7}
Ethyl acetate	1.25×10^{-8}	4.53×10^{-8}	8.43×10^{-8}	2.34×10^{-7}
Propyl acetate	7.24×10^{-9}	2.94×10^{-8}	4.64×10^{-8}	1.45×10^{-7}
Dichloromethane	3.34×10^{-8}	9.81×10^{-8}	1.86×10^{-7}	4.42×10^{-7}
Chloroform	8.70×10^{-9}	2.81×10^{-8}	6.12×10^{-8}	1.27×10^{-7}
Acetone	2.37×10^{-8}	7.90×10^{-8}	1.36×10^{-7}	3.49×10^{-7}
MMA	7.01×10^{-9}	2.86×10^{-8}	5.25×10^{-8}	1.63×10^{-7}
BMA	2.55×10^{-9}	1.17×10^{-8}	2.30×10^{-8}	8.68×10^{-8}

The diffusion coefficients (D_p) of methanol, ethanol, propanol, butanol, methyl acetate, ethyl acetate, propyl acetate, dichloromethane, trichloromethane, acetone, methyl methacrylate, butyl methacrylate at 150, 170, 180, 200 °C were determined at infinite dilution and tabulated in Table 7.

The diffusion coefficients were correlated with the free volume theory to analyze the temperature dependence of diffusion coefficients. The free volume parameters for PMMA co BMA were determined using the data reported by Tonge et al. [24]. Tonge et al. calculated the pure PMMA and PBMA free volume parameters using viscosity versus temperature data. Free volume parameters of PMMA co BMA were calculated using the mixing rule and found as $K_{22} = 93.44$ K, $K_{12}/\gamma_2 = 1.4 \times 10^{-4}$ cm³/gK, $V_2^* = 0.7659$ cm³/g [24]. All diffusion data were regressed using two fitting parameters, D_0 and ξ , using non linear regression analysis.

The comparison of experimental diffusion coefficients and the correlated values with the free volume theory are shown in Figs. 6–9. The data were well correlated with Vrentas Duda free volume theory. These figures pointed out that besides tem-

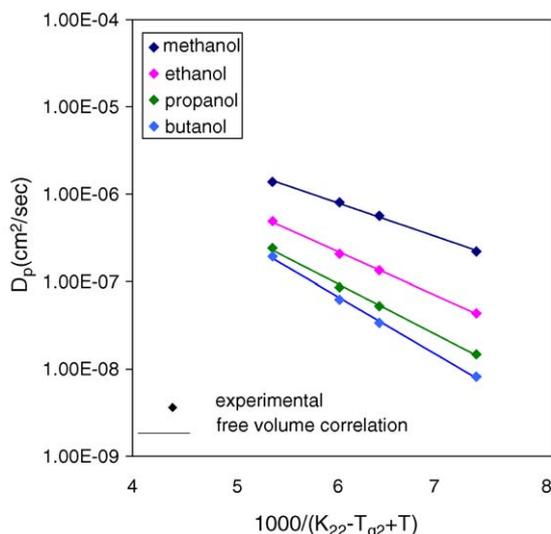


Fig. 6. Temperature dependence of D_p for alcohols-PMMA co BMA system.

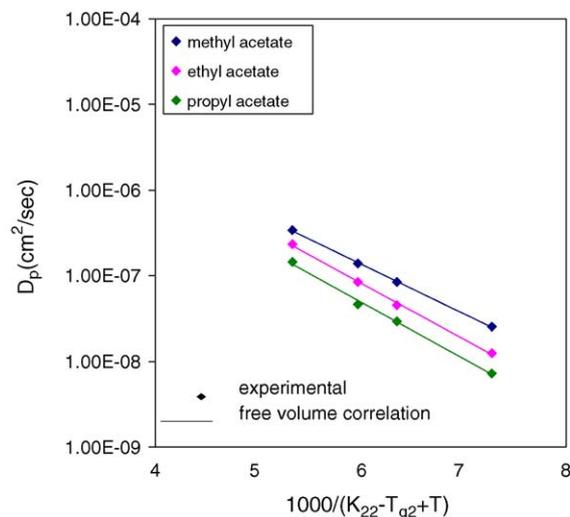


Fig. 7. Temperature dependence of D_p for acetates-PMMA co BMA system.

perature effect on D , molecular size had an effect on diffusion coefficient. As molecular size increased, diffusion coefficient decreased.

The regressed parameters (D_{01} and ε) of PMMA co BMA-solvent systems were tabulated in Table 8. From Table 8 and Fig. 10, one can also see that with increasing molecular size of the solvent molecule, D_0 and ξ also increased.

In literature, to our knowledge, no one studied the diffusion or thermodynamic properties of PMMA co BMA polymer-solvent system. Diffusion data of MMA and BMA monomers in PMMA and PBMA homopolymers were studied using the pulsed field gradient (PFG)-NMR sorption technique by Tonge et al. [24]. They obtained the self diffusion coefficients at 298 and 313 K. The diffusion coefficients of MMA in PMMA at 298 and 313 K were in the range of 3×10^{-9} – 0.5×10^{-10} m²/s in the polymer weight fraction of 0–0.4. The diffusion coefficients of MMA in

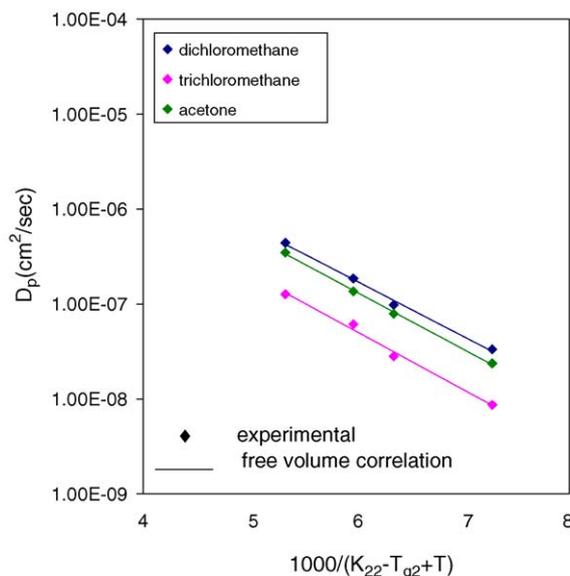


Fig. 8. Temperature dependence of D_p for dichloromethane, trichloromethane, acetone in PMMA co BMA.

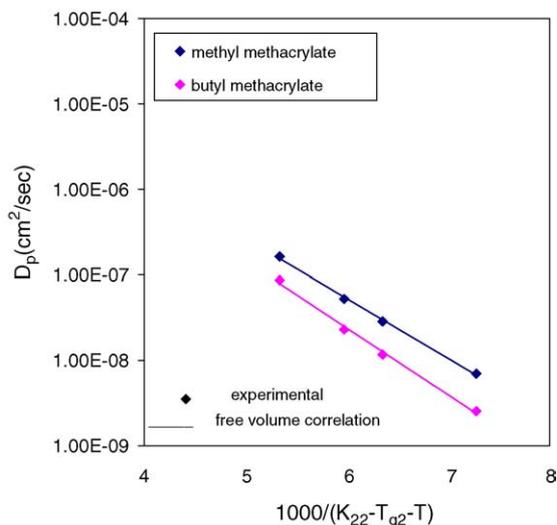


Fig. 9. Temperature dependence of D_p for MMA, BMA in PMMA co BMA.

Table 8
Free volume parameters for various solvents

Solutes	D_0 (cm ² /s)	ξ
Methanol	2.28×10^{-04}	0.17
Ethanol	3.54×10^{-04}	0.23
1-Propanol	4.59×10^{-04}	0.26
1-Butanol	1.06×10^{-03}	0.29
Methyl acetate	4.11×10^{-04}	0.24
Ethyl acetate	6.96×10^{-04}	0.27
Propyl acetate	4.63×10^{-04}	0.28
Dichloromethane	5.35×10^{-04}	0.24
Trichloromethane	2.38×10^{-04}	0.26
Acetone	5.37×10^{-04}	0.25
MMA	8.44×10^{-04}	0.29
BMA	1.20×10^{-03}	0.33

PBMA was in the range of 3.5×10^{-9} – 1×10^{-9} m²/s at 298 K and 6×10^{-9} – 1×10^{-9} m²/s at 313 K in the polymer weight fraction of 0–0.4. In the same polymer weight fraction, D_p of BMA in PBMA was in the range of 1.5×10^{-9} – 0.4×10^{-9} m²/s at 298 K and 1.3×10^{-9} – 0.5×10^{-9} m²/s at 313 K. Also, Arnould [25] reported diffusion of various solvents (methanol, acetone, methyl acetate, ethyl acetate, propyl acetate) in

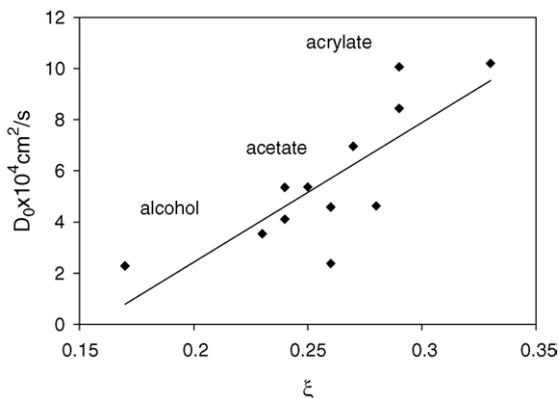


Fig. 10. Effect of molecular size on D_0 and ξ .

PMMA homopolymer at infinite dilution of solvent and they have obtained diffusion coefficients in the range of 1.29×10^{-7} – 7.22×10^{-10} cm²/s at 433–343 K.

5. Conclusion

Polymer–solvent interactions, partition and diffusion coefficients at infinite dilution of solvent were obtained for various solvents in poly(methyl methacrylate co butyl methacrylate) (PMMA co BMA) by inverse gas chromatography (IGC). Since IGC technique is rapid, simple, 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 revealed useful information about the degree of compatibility between the polymers and the various solvents used. The weight fraction activity coefficient Ω_1^∞ , Flory–Huggins interaction parameters χ of various solvents in PMMA co BMA were determined and trichloromethane and dichloromethane were obtained as the most suitable solvents for the polymer. The solubility parameters of both solvents (δ_1) and polymers (δ_2) the polymer were also estimated. The prediction of the degree of compatibility of the various solvents with PMMA co BMA 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. [5] for calculating the partition and diffusion coefficients of solvents in polymers at infinite dilute 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 where as diffusion coefficient increased. Vrentas–Duda free volume theory was used to correlate the diffusion coefficients and free volume parameters of various solvents in PMMA co BMA polymer were calculated by regression method. The results indicated that the diffusion data were well correlated by the free volume theory.

List of symbols

C	solute concentration in the gas phase (mol/cm)
C'	solute concentration in polymer phase (mol/cm)
D	mutual diffusion coefficient (cm/s)
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
K_{11}	solvent free-volume parameter (cm/g K)
K_{21}	solvent free-volume parameter (K)
K_{12}	polymer free-volume parameter (cm/g K)
K_{22}	polymer free-volume parameter (K)
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)
V_{FH}	specific hole-free volume (cm/g)
V_i^*	specific critical hole free volume of component i (cm/g)
z	axial direction

Greek letters

α	nondimensional thermodynamic parameter
β	nondimensional polymer phase diffusion parameter
γ	overlap factor which accounts for shared free volume
Γ	nondimensional gas phase diffusion parameter
δ_i	solubility parameter (J/cm ³) ^{1/2}
ξ	ratio of solvent and polymer jumping units
τ	film thickness in the capillary column (cm)
χ	Flory–Huggins polymer–solvent interaction parameter
Ω_i	weight fraction of component i

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