Organic Vapor Sorption by Copolymers of Poly(styrene-butadiene) Using a Quartz Crystal Microbalance

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Abstract

Knowledge of the solubilities of solvents in polymers is needed for the design as well as operation of polymer processing plants to meet environmental, health and safety regulations. Solubility data for copolymer systems are rare in literature, especially for systems with polar solvents. Solubilities of benzene, hexane, dichloroethane, and chloroform in copolymers of poly(styrene-butadiene) at 295.15 K are presented in this study. Literature data exist for pure polymers of poly(styrene) and poly(butadiene) for some of these solvents; however, copolymer data are unavailable. The copolymers investigated had compositions of twenty-one percent, forty-five percent, and eighty-five percent of poly(styrene) in poly(butadiene). The experiments were conducted using a quartz crystal microbalance (QCM) along with a flow-type, vapor generation apparatus. Quartz crystal parameters were measured using an impedance analyzer (Agilent 4294A) to allow for equivalent circuit analysis of the coated and solvent-exposed crystal. These parameters were utilized to establish the mass-balance regime of the QCM to gather thermodynamic sorption data. Solvent activities were represented with a modified Flory-Huggins model to within experimental error. Free volume activity coefficient models should adequately represent sorption at these low pressures, hence, the applicability of several free volume models to the polymer solvent systems was determined by a comparison of these model solubility predictions to experimental results. These models were UNIFAC-FV, Entropic-FV, and GK-FV and can be found in references [1, 2, and 3]. The Flory Huggins model combinatorial term does not account for free volume changes, however, these free volume models account for the changes in the free volume due to mixing solvents and polymers. UNIFAC-FV and Entropic-FV models were tested for their accuracy in predicting solubilities of polar and nonpolar systems.

1. Introduction

Knowledge of the solubilities of solvents in polymers is needed for the design as well as operation of polymer processing plants to meet environmental, health and safety regulations. Solubility data for copolymer systems are rare in literature, especially for systems with polar solvents [1]**.** Polymer vapor sorption has been studied using techniques of vapor pressure lowering, isopiestic sorption, inverse gas liquid chromatography, and quartz crystal microbalances (QCM). Bawn and Wajid have reported several accurate results using the vapor lowering technique [2]**.** The quartz crystal microbalance technique has several advantages over the many other techniques: shorter equilibrium times, applicability to finite concentrations, reliability, and accuracy. Accurate and reliable polymer vapor sorption studies using the quartz crystal microbalance method have been reported by us and others previously [3-7]**.** We report solubilities of four solvents in copolymers of poly(styrene-butadiene) in the concentrated polymer regime. The effect of polymer composition on solubility was also studied. The effect of polarity on solubility was also determined by proper selection of the solvents.

Polar and nonpolar solvent vapors were generated using a newly designed vapor generation apparatus. The copolymers were investigated in their rubbery state at 294.15 K.

2. Experimental Section

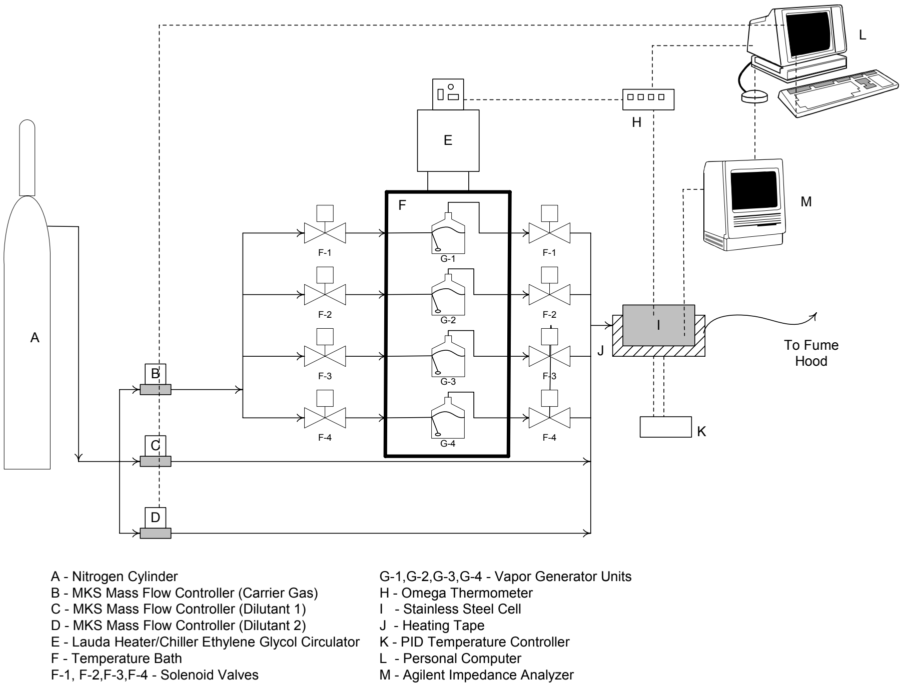
Materials

Solvents were obtained from Acros Chemicals. All solvents were HPLC grade with 99.99 % purity. Poly(styrene-butadiene) copolymers of several compositions were obtained from different sources: that with 45% and 21% polystyrene was obtained from Acros whereas poly(styrene-butadiene) with 85% polystyrene was obtained from Polysciences. The average molecular weight of the 45% polystyrene sample, (PSB 45% S), is not known, however, it is of high molecular weight. The average molecular weight of the 21% polystyrene sample, (PSB 21% S), was 400,000; the average molecular weight of the 85% polystyrene sample, (PSB 85% S), was 109,300. Finally, nitrogen carrier gas, which was used in generating test vapor samples of the solvents, was ultra high purity grade. QCMs, with fundamental frequencies of 10 MHz, were obtained from International Crystal Manufacturing.

Experimental Apparatus

There were two essential parts of the experimental apparatus: The vapor generation equipment and the QCM. QCM operational theory, as applied to polymer sorption studies has been described previously [7]. Generation of the solute vapor was an essential part of the experiment. Standard gases can be generated precisely using established vapor generation techniques [8, 9]. The apparatus used to generate the organic vapors is shown in Figure 1.

Figure 1. Vapor Generation Apparatus



Organic liquids were contained in the four bubbler units, G1 to G4, housed in a water bath and connected to a Lauda water circulator for temperature control. MKS mass flow controllers (B, C, and D) were used to regulate nitrogen carrier gas through these bubbler units. Multiple mass flow controllers allowed for a variation of test sample concentrations. In the present design, there were three flow streams: The carrier stream (through MFC B) passing through the bubbler, and the dilutant streams (through MFCs C and D). To generate a vapor sample, a bubbler unit was selected by activating a pair of solenoid valves (F1 to F4).

Pure nitrogen gas flowed through a sparger, which allowed for improved mass transfer into the vapor phase. An Agilent 4294A precision impedance analyzer was used to monitor the resonant frequency and equivalent circuit parameters of the QCM housed in the stainless steel flow cell (I). The cell temperature was maintained at a fixed temperature using a PID temperature controller. The QCM device was attached to a custom made printed circuit board using a commercially available socket holder for 10 MHz QCMs. The apparatus was completely automated using a National Instruments data acquisition card (PCI 6025E), a GPIB controller, and Labview programming. The vapor pressure of the liquid at the bubbler temperature was calculated using an accurate vapor pressure correlation, Wagner's equation.

$$\ln\left(\frac{P_{vp}}{P_c}\right) = \left((1-x)^{-1} * \left(V_{PA} * x + V_{PB} * x^{1.5} + V_{PC} * x^3 + V_{PD} * x^6\right)\right) \qquad (1)$$

Where $x = 1 - \frac{T}{T_c}$.

Table 1. Constants in Wagner's equation

Solvent	V_{PA}	V_{PB}	V_{PC}	V_{PD}
BNZ	-6.98270	1.33210	-2.6286	-3.3340
HXN	-7.46765	1.44211	-3.2822	-2.5094
DCE	-7.36864	1.76727	-3.3429	-1.4353
CLF	-6.95546	1.16625	-2.1397	-3.4442

P_c is the critical temperature and P_{vp} is the vapor pressure of the solvent in torr. T is the solvent temperature or system temperature, and T_c is the critical temperature in Kelvin (K). Constants V_{PA}, V_{PB}, V_{PC}, and V_{PD} for the Wagner's equation were obtained from literature and are shown in Table 1 [10]. The solvents will be abbreviated by the following convention: benzene (BNZ), n-hexane (HXN) dichloroethane (DCE) and chloroform (CLF).

Experimental Procedure

The procedure for generating vapor samples was described in the previous section. The polymer must be coated onto the QCM surface prior to experimentation. The procedure for coating the QCM is described here. The uncoated QCM was thoroughly cleaned with deionized water, acetone, and chloroform, and then dried with nitrogen gas. Next it was placed in a Harrick plasma cleaner for 15 minutes to remove any further contaminants. This procedure also aids in removing de-wetting effects [11]. The frequency of the uncoated crystal at the desired temperature, 295.15 K was then recorded. Poly(styrene-butadiene) was dissolved in chloroform to make a solution containing 0.1 wt% copolymer . The copolymers were coated onto the QCM using a spray coating technique [12]**.** The thickness of the coating was determined by experimental trial and error procedures to be in the vicinity of 5 kHz. This meant that the polymer coating caused a decrease in the resonant frequency of the QCM of approximately 5 kHz. According to the QCM principles of operation, coatings should be ideally thin [12]. The film was annealed and the coated QCM was allowed to cool to desired operating temperature. The change in the frequency Δf_0 from the bare crystal at the experimental temperature was recorded. After achieving the desired solvent cell temperature and bubbler temperature (15 ˚C) UHP nitrogen was used to generate vapors of desired concentrations as described previously. The vapor mixture was then allowed to pass thorough the flow cell, resulting in a change in the frequency of the crystal which was continuously logged into an Excel spreadsheet. After sorption of the solute vapor, pure nitrogen gas was passed over the coated QCM to allow complete desorption of the vapors. The procedure was repeated for varying concentrations of the vapor for different solvents. Equilibrium times for (PSB 21% S) and (PSB 45% S) were experimentally determined to be about 10 minutes. Equilibrium times for (PSB 85% S) were experimentally determined to be about 15 minutes.

3. Activity Model

Activities of the solvents in the polymer phase were calculated by assuming that the vapor phase is a mixture of solvent and nitrogen (no polymer) and that the vapor phase compressibility is given by the virial equation of state, truncated after the second virial coefficient:

$$Z = 1 + \frac{B_{mixt}}{RT} \tag{3}$$

Where B_{mixt} is the virial coefficient for the mixture of nitrogen and the solvent vapor, *R* is the gas constant and *T* is the temperature. The fugacity of the solvent in the vapor phase is then given by

$$f_1^{\,v} = P_1 Exp\left[\frac{P}{RT}\left(B_{11} + y_3^2\left(2B_{13} - B_{11} - B_{33}\right)\right)\right] \tag{4}$$

Here B_{11} and B_{33} represent the second virial coefficients of the pure solvent and nitrogen, respectively. The second cross virial coefficient is represented by B_{13}. Second virial coefficients, at 298.15 K, were obtained from the Tsonopoulos correlation, and are given in Table 2 [13]. The second virial coefficient for nitrogen was calculation from Tsonopoulos correlation to be -5.9170 cm^3/mole. P_1 is the partial pressure of the solvent.

The fugacity of the pure solvent was determined by applying the Poynting correction to the saturated vapor fugacity, approximated with the truncated virial equation of state after the second virial coefficient. Equating the fugacities of the solvent in the liquid and vapor phases allows for determining the experimental activity of the solvent in the polymer.

Table 2. Second virial coefficients at 295.15 K

Solvents	*B_{11} (cm^3/mole)*	*B_{13} (cm^3/mole)*
BNZ	-1731	-155
HXN	-2024	-172
DCM	-1810	-147
CLF	-1296	-136

$$a_1 = \left(P_1 \exp\left[\frac{P}{RT}(B_{11} + y_3^2(2B_{13} - B_{11} - B_{33}))\right]\right) \Big/ \left(P_1^{Sat} \exp\left[\frac{B_{11}P_1^{Sat}}{RT}\right] \exp\left[\frac{V_1^{Sat}}{RT}(P - P_1^{Sat})\right]\right) \tag{5}$$

Where *P* is the total pressure of the system, P_1^{Sat} is the saturated vapor pressure of the solvent at the system temperature T, P_1 is the partial pressure and V_1^{Sat} is the saturated liquid molar volume of the solvent, which was calculated using the modified Rackett equation [10]. Data were fitted to the Flory-Huggins activity model for which the Gibbs excess energy is given by:

$$\frac{nG^E}{RT} = N_1.\ln\frac{\Phi_1}{X_1} + N_2.\ln\frac{\Phi_2}{X_2} + \chi\Phi_1\Phi_2(N_1 + rN_2) \tag{6}$$

Where N_i is the number of moles, X_i is the mole fraction, and Φ_i is the volume fraction of the solvent and polymer for *i* =1 and 2, respectively. The ratio of the molecular volumes, V_2/V_1 is represented by *r.* V_1 and V_2 were obtained from the van der Waals volumes, which were estimated by summing the group volumes given by Bondi [14, 15], shown in Table 3. The group volume for (PSB 21% S) was determined to be 17758 by using the weight averaged molecular weight; the group volume for (PSB 45% S) was 17196, and the group volume for (PSB 85% S) was 4443. The volume fraction of each component can be expressed in terms of these van der Waals volumes by Equation 7 below. Values for the van der Waals group volumes are given in Table 3 for the solvents studied.

$$\Phi_i = \frac{V_i X_i}{\sum V_i X_i} \tag{7}$$

The Flory-Huggins interaction parameter χ is often not constant, as is the case with most of our experimental data. To represent the experimental data for such cases within estimated experimental accuracies, we have assumed a linear dependence of χ on volume fraction as given by equation 8.

$$\chi = A\Phi_1 + B\Phi_2 \tag{8}$$

Table 3. van der Waals volume parameters

Solvents	V_i
BNZ	3.1878
HXN	4.4998
DCE	4.1212
CLF	2.8700

This assumed linear dependence was found to represent the experimental data within experimental accuracies. The χ parameter was used as a measure of the strength of interaction between the sorbed vapor and the polymer film. Hence, χ could be used as a guide to predict polymer/ solvent compatibility. Using this linear dependence yields the following expression for the solvent activity:

$$\ln a_1 = \ln(1-\Phi_2) + \left(1-\frac{1}{r}\right)\Phi_2 + [2.(A-B)\Phi_1 + B]\Phi_2^2 \tag{9}$$

Experimental solvent activity data were fitted to these activity models by minimizing the solvent weight fraction sum of squares:

$$\sum (w_{1,\exp t} - w_{1,calc})^2 \tag{10}$$

Each sorption data point was given equal weight in this regression. Weight fraction was utilized as the fitted (dependent) variable because it is the experimentally measured quantity. In the regression process, $w_{1,calc}$ was obtained by first solving Equation 10 by iteration for solvent volume fraction, and then converting it to weight fraction for each experimental value of solvent activity, a_1. A nonlinear least-squares data fitting by the Gauss-Newton method in Matlab, with a Levenberg–Marquardt type adjustment, was used to estimate the coefficients. Calculated average absolute deviations (residuals) were found to be small. The resulting two parameter fits represented the data to within experimental uncertainty. Values of the fitted parameters and associated confidence intervals are given in the next section.

4. Experimental Results and Discussion

Results are presented for the experimental activity of benzene, n-hexane, dichloroethane, and chloroform at 295.15 K in the three copolymers in Figures 2 to 4. Equilibrium could not be reached in 15 minutes for the hexane/(PSB 85% S) system, consequently, data for this system are absent. The resistance of the TSM equivalent circuit as the polymer film was exposed to increasing percentage levels of solvent. The film resistance provides information about the visco-elastic nature of the film. For the activity data to be thermodynamically correct, the QCM must function solely as a mass balance. Visco-elastic contributions to the total frequency shift result when the QCM is no longer in the mass balance regime. Resistance values were monitored using the Agilent impedance analyzer. Sorption data at resistance changes above 50 ohms were arbitrarily neglected. Since literature data on polystyrene-butadiene copolymer systems do not exist, no comparison of our experimental results could be made with literature data.

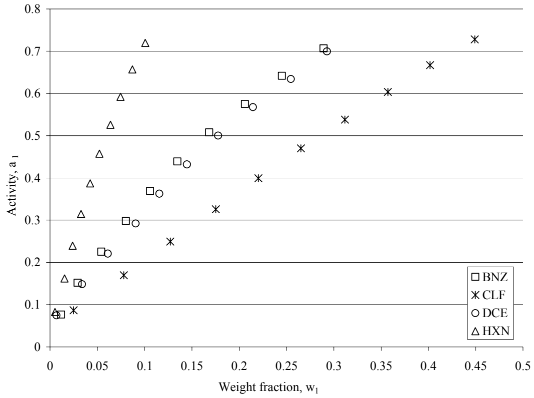


Figure 2. Activity of Solvents in (PSB 21% S)

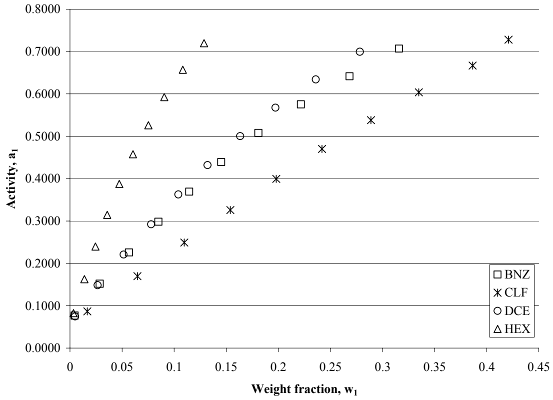


Figure 3. Activity of Solvents in (PSB 45% S)

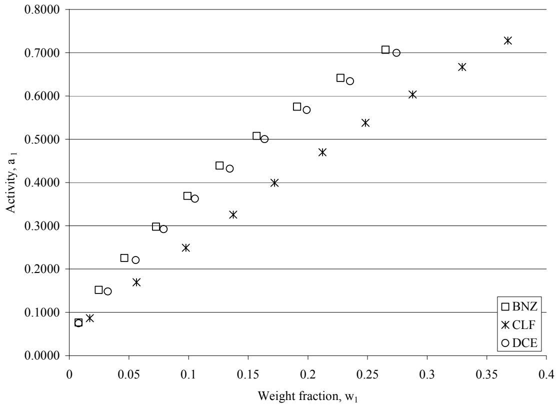


Figure 4. Activity of Solvents in (PSB 85% S)

In the discussion section, experimental results were compared with the predictive and correlative models of UNIFAC-FV, Entropic-FV, GK-FV and the Flory-Huggins model. As the percentage of polystyrene composition increases in the poly(styrene-butadiene) copolymer, the rubbery nature increases; consequently, (PSB 85% S) is a more rigid copolymer. Equilibrium times for (PSB 85% S) were adjusted to 15 minutes and the polymer film thickness was reduced, as opposed to 10 minutes for (PSB 21% S) and (PSB 45% S).

The maximum fluctuation in frequency, which is the amount of noise present in the resonant frequency after equilibrium is achieved, varied. When exposed to organic solvents it was observed that these fluctuations increased with solvent concentration. The errors introduced in weight fractions with these fluctuations are on the order of 0.0001 to 0.001.

From Figures 2 to 4 we see that chloroform has lower solvent activity in all three copolymers and hexane has the highest activity in (PSB 45% S) and (PSB 21% S). It was difficult to determine the differences in activity of benzene and dichloroethane. The effect of polarity on solubility could not be determined because dichloroethane had similar activities to benzene but different activity from chloroform. A comparison of each of the solvents in all three polymers did not show any significant distinction of activity, consequently the effect of styrene composition on solubility could not be determined.

Table 4. Predictive Models

Solvents	Unifac-FV	GK-FV	Entropic-FV
	85 % Styrene		
Benzene	10.2	10.38	11.51
Dichloroethane	11.72	8.75	21.00
Chloroform	11.93	36.11	21.04
n-hexane	***	***	***
	45 % Styrene		
Benzene	55.25	25.8	25.84
Dichloroethane	47.96	21.42	18.45
Chloroform	58.64	70.66	61.09
n-hexane	50.71	51.54	58.38
	21 % Styrene		
Benzene	***	25.91	25.64
Dichloroethane	***	48.42	45.98
Chloroform	***	***	***
n-hexane	56.67	55.96	60.28

The predictive capability of UNIFAC-FV, Entropic-FV and GK-FV models for these polymer systems was also determined. A comparison with all three models for each solvent/copolymer system is shown in Table 4. These results are presented as the percent average absolute deviations between experimental and model-predicted activities for each solvent. Results indicate that UNIFAC-FV is a poor predictive model for the systems in which the percentage levels of poly(butadiene) is high. UNIFAC-FV, GK-FV and Entropic-FV are good predictors of solubility for systems in which poly(styrene) composition is high. In addition to the free volume models, the Flory-Huggins model was also compared to experimental results. The model parameters, A and B, are listed in Table 5, which also lists the lower (*l*) and upper (*u*) 95% confidence bounds on the regressed parameters. The percent absolute average deviations (AAD) between fitted model and experimental data are also listed in this table.

Table 5. Flory-Huggins Parameters

			95 % Confidence Interval			
			A		B	
Solvent	*A*	*B*	*l*	*U*	*l*	*u*
			21 % S			
BNZ	0.2012	0.6225	0.0265	0.3758	0.5287	0.7162
CLF	0.3281	0.3349	0.1690	0.4872	0.2267	0.4431
DCE	0.2661	0.4462	0.0261	0.5061	0.3054	0.5869
HXN	0.8437	1.4826	0.5028	1.1845	1.4271	1.5381
			45 % S			
BNZ	0.0772	0.5488	-0.1925	0.3470	0.3836	0.7139
CLF	0.2889	0.4740	0.0693	0.5085	0.3360	0.6120
DCE	0.2062	0.5749	-0.0849	0.4973	0.4160	0.7338
HXN	0.4085	1.2018	-0.0174	0.8345	1.0877	1.3159
			85 % S			
BNZ	0.1984	0.6343	-0.0717	0.4685	0.4900	0.7786
CLF	0.4995	0.5322	0.2746	0.7245	0.4110	0.6534
DCE	0.2572	0.467	0.0568	0.4575	0.3508	0.5832

5. Conclusions

Experimental activities of benzene, n-hexane, dichloroethane and chloroform were determined in polystyrene-butadiene copolymers. Results indicate that UNIFAC-FV is a poor predictive model for the systems in which the percentage levels of poly(butadiene) is high. UNIFAC-FV, GK-FV and Entropic-FV are good predictors of solubility for systems in which poly(styrene) composition is high. Plots of activity *vs* weight fraction calculated from the theoretical free volume models show that activity should decrease with increasing styrene concentration in the copolymer. Since these models failed to compare well with experimental data it is difficult to determine the effect of styrene composition on activity. Additionally, experimental activities of benzene and dichloroethane in (PSB 45% S) and (PSB 85% S) were too close to determine the activity trends. Trends for chloroform could not be established because all three predictive models failed for (PSB 21% S). Finally, trends for n-hexane could not be established because equilibrium times were longer than 15 minutes we have allowed, and data have not yet been obtained for the (PSB 85% S)/n-hexane system.

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