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Sorption of Benzene, Toluene, and Ethylbenzene at Low Concentrations by Plasticized Poly(ethyl methacrylate) and Polystyrene Polymers Using a Quartz Crystal Microbalance at 298.15 K

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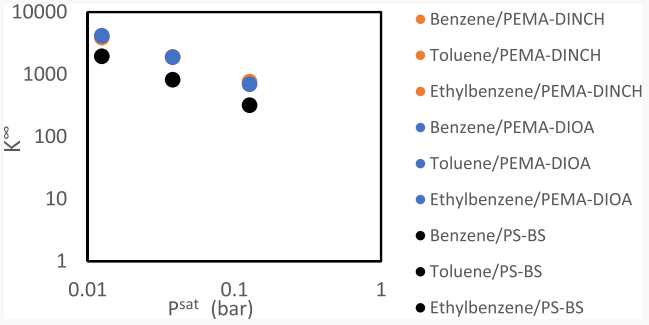
ABSTRACT: Solubilities of benzene, toluene, and ethylbenzene in plasticizing poly(ethyl methacrylate) with diisononyl cyclohexane-1,2-dicarboxylate and diisooctyl azelate and in polystyrene with *n*-butyl stearate are reported in the form of activity versus weight fraction data, measured using a quartz crystal microbalance at 298.15 K. Measured concentrations of benzene, toluene, and ethylbenzene in the films are in the range of 0 to approximately 1.0 weight percent and are used to estimate infinite dilution activity coefficients of these solvents in the plasticized polymers.



INTRODUCTION

Solubility data of organic compounds in polymers and copolymers from the quartz crystal microbalance (QCM) have produced interesting thermodynamic results and interpretation.[1−6] In this study, we present solubilities of benzene, toluene, and ethylbenzene (BTEX compounds, along with xylenes) in plasticized poly(ethyl methacrylate) (PEMA) and polystyrene (PS) at 298.15 K using a QCM equipped with a new vapor generation system to target low concentrations. As part of the continuing study on the effect of added plasticizers on solvent sorption, three plasticizers, diisononyl cyclohexane-1,2-dicarboxylate (DINCH), diisooctyl azelate (DIOA), and *n*-butyl stearate (BS), have been added to the homopolymers of PEMA and PS. It has been previously reported[3,7−9] as to how the addition of plasticizers modifies the chemical and physical properties of glassy polymers and further improves the sorption of organic species. In this study, the effect of plasticization is evaluated by collecting sorption data and extracting the infinite dilution partition coefficient values from these data.

Detection and quantification of volatile organic compounds (VOCs) is important because of the health impacts they have on the human body ranging from nausea and headaches to cancer.[10−12] Among the VOCs, benzene, toluene, ethylbenzene, and xylenes are the chemicals which need to be monitored on a regular basis.[13−15] In this work, a polymer−plasticizer film has been employed as the sensor film using a QCM to study the solubilities of these analytes. Plasticizers have been used previously and have been shown to alter the physical and chemical properties of the polymer by enhancing the sensitivity and improve diffusivity.[3,7,9,16] Sorption of benzene, toluene, and ethylbenzene in plasticized PEMA with DINCH and DIOA plasticizers has been reported previously[3] for plasticizer concentrations in the range of 10−25 wt % and solvent concentrations in the range of approximately 0.05−0.6 wt %. There have been no published data for sorption of the solvents used herein for the PS−BS mixture.

EXPERIMENTAL SECTION

Materials. PEMA with a molecular weight of 340,000 g/mol and PS with a molecular weight of 280,000 g/mol were purchased from Sigma-Aldrich and were used as supplied. The three plasticizers studied were DINCH, BS, and DIOA. DINCH (424 g/mol) was provided by BASF, while DIOA (412 g/mol) and BS (340.60 g/mol) were obtained from Scientific Polymer Products Inc. Benzene, ethylbenzene, and

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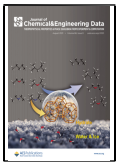

Table 1. IUPAC Names, Abbreviations, CAS Numbers, Purities, and Supplier Information for the Chemicals Used in This Work

IUPAC name	abbreviations	CAS reg. no.	purity (w/w) (%)	supplier
benzene	benzene	71-43-2	≥99.9	Sigma-Aldrich
toluene	toluene	108-88-3	≥99.9	Sigma-Aldrich
ethylbenzene	ethylbenzene	100-41-4	≥99.9	Sigma-Aldrich
PEMA	PEMA	9003-42-3		Sigma-Aldrich
PS	PS	9003-53-6		Sigma-Aldrich
DINCH	DINCH	166412-78-8		BASF
DIOA	DIOA	26544-17-2		Scientific Polymer Products Inc.
BS	BS	123-95-5		Scientific Polymer Products Inc.

toluene (99% purity) were purchased from Sigma-Aldrich and used without any further purification. Complete chemical information is provided in Table 1. Molecular weights, molar volumes, glass-transition temperatures, and melting points of the materials used in this study are given in Table 2. AT-cut quartz crystals with a 5 MHz resonant frequency were used, which were supplied by Philips Technologies.

Table 2. Molar Masses, Volumes, Glass-Transition Temperatures, and Melting Points for the Chemical Species Used in This Study

compound	molar mass (M_i g/mol)	molar volume (V_i mL/mol)	glass-transition temperature (K)	melting point (K)
benzene	78.11	89.17		
toluene	92.14	105.91		
ethylbenzene	106.97	123.52		
PEMA	340,000	306,300	338.15	518.15
PS	280,000	266,666.67	373.15	543.15
DINCH	424.6	446.95		
DIOA	412.65	455.97		
BS	340.60	400.71		

Apparatus and Procedure. Compared to the QCM apparatus utilized in our previous work,[2] the current setup used for studying the sorption behavior at low activities is modified in how dilutions are achieved. The working apparatus for this experiment consists of a stream of solvent vapors being diluted with the carrier gas (ultra-high-purity nitrogen) reaching the oscillating 5 MHz QCM sensor by controlling the flow rates of nitrogen and the solvent. The nitrogen carrier gas is fed through an MKS mass-flow controller (MFC1) at a constant flow rate of 100 sccm, while the solvent flow rate is controlled using an automated syringe pump as shown in the schematic in Figure 1. The nitrogen gas passes through a heat exchanger (HX1), which is kept at constant temperature by using a NESLAB RTE 740 chiller (chiller 1). At the end of this first heat exchanger, the solvent is supplied to the gas stream through a gastight syringe (Hamilton) with a cemented needle which is automated using a Harvard Pump 11 Pico Plus Elite apparatus, which provides an option to use the constant syringe withdraw flow rate or to set up multiple flow rates separated with a delay time that will provide enough time for the QCM crystal to condition to its original state. The mixture of the nitrogen gas and the solvent vapor of the desired concentration passes through the second heat exchanger (HX2) which is maintained at 25 °C using chiller 2 and finally reaches the QCM crystal oscillating at 5 MHz. It must be noted that the solvent leaving the syringe is completely vaporized because of the nitrogen flow and the temperature being maintained by the chiller. When the solvent vapors reach the crystal and their sorption on a polymer-coated QCM crystal begins, the frequency of the crystal sensor drops following the Sauerbrey equation[17]

$$w_1 = \frac{\Delta f}{\Delta f + \Delta f_0} \tag{1}$$

where w_1 is the weight fraction of the solvent in the polymer, Δf refers to the frequency shift from the unexposed polymer to the polymer plus sorbed solvent, and Δf_0 refers to the frequency change between the bare crystal and the crystal coated with the unexposed polymer. After the crystal has equilibrated and sorption has taken place, the Harvard pump is paused and 100 sccm of pure nitrogen is allowed to flow over the crystal for it to reach its polymer-coated frequency. After the crystal has reached this frequency, the withdrawal flow rate of the pump is altered to get a new solvent concentration. The frequency response signal from the crystal travels to a Maxtek PLO-10i phase locked oscillator and from there to a Hewlett Packard 5334B counter that measures the frequency. The time (in seconds) and frequency (in Hz) data are recorded with a LabView program on a computer.

Thin films composed of polymer−plasticizer blends of thicknesses on the order of a few microns were spin-coated on the surface of the QCM crystal. The blend of the polymer and plasticizer is prepared gravimetrically by adding the desired amount of the plasticizer (5% for DINCH, DIOA with PEMA, and 15% for BS with PS) to the polymer, which is dissolved in the chloroform solvent, sonicated for an hour, and left overnight before being spin-coated onto the QCM. The desired percentage amounts of plasticizers used in this work were chosen so that solubility enhancement is observed without any viscoelastic effects. The uncertainty in calculated solvent activity can be found by the following equation:

$$\frac{\sigma_{a_1}}{a_1} = \frac{\sigma_{n_s}}{n_s} + \frac{\sigma_{n_N}}{n_N} + \frac{\mathrm{d}\ln P_1^s}{\mathrm{d}T}\sigma_T \tag{2}$$

where σ_{a_1} is the uncertainty in the calculated solvent activity, P_1^s is the saturated vapor pressure of the solvent, σ_T is the uncertainty in the cell temperature found to be 0.01 K, σ_{n_s} is the uncertainty in the solvent flow rate found to be 0.35%, σ_{n_N} is the uncertainty in nitrogen flow rate found to be 1%. The resultant uncertainty in calculated solvent activity was found to be less than 2%. To calculate the uncertainty in solvent weight fraction, eq 3 was used as follows:

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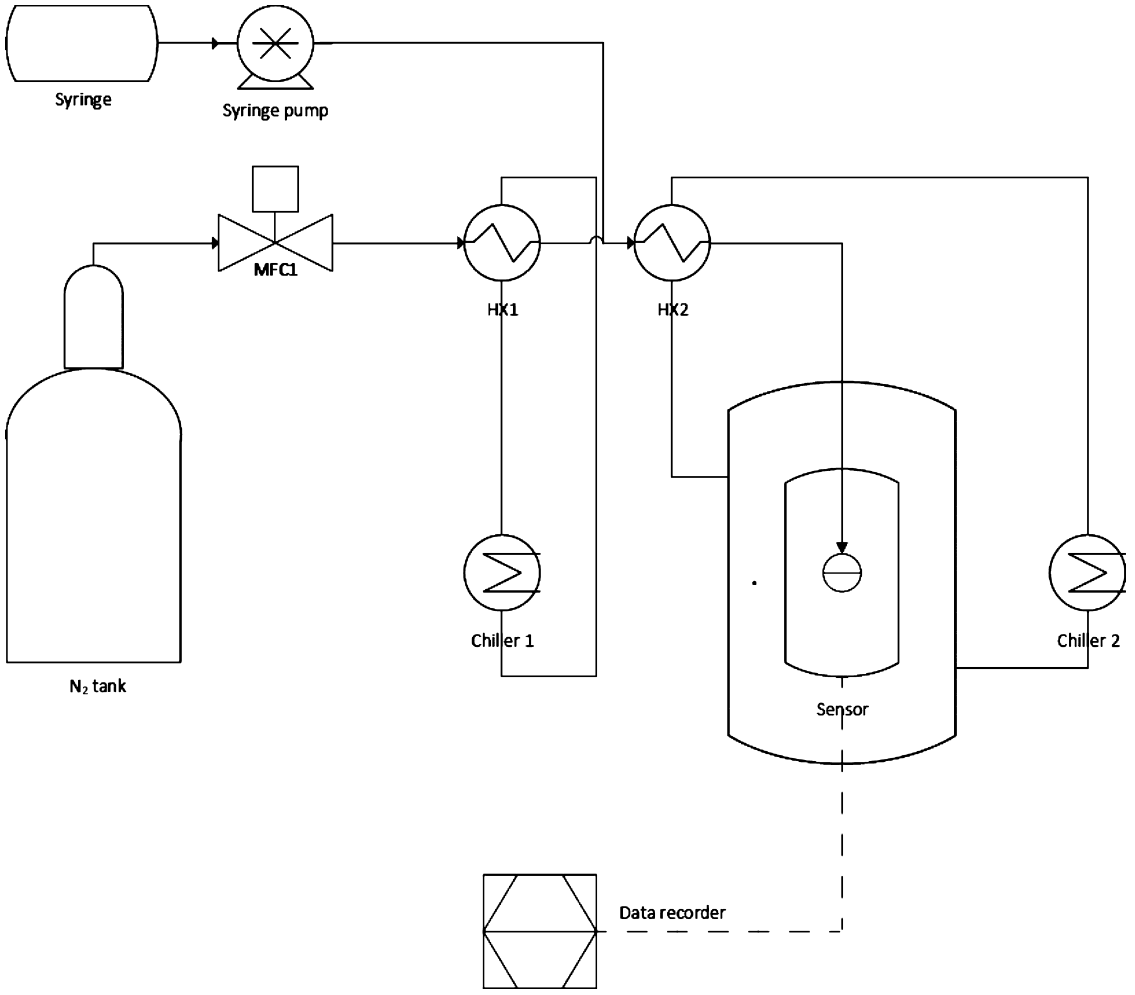

Figure 1. Schematic diagram of the QCM apparatus.

$$\sigma w_1 = \frac{\frac{\sigma\Delta f}{\Delta f_0} + \left(\frac{w_1}{1-w_1}\right)\left(\frac{\sigma\Delta f_0}{\Delta f_0}\right)}{\left(1 + \frac{w_1}{1-w_1}\right)} \quad (3)$$

where w_1 is the weight fraction of the solvent in the polymer and $\sigma_{\Delta f}$ and $\sigma_{\Delta f_0}$ are uncertainties in frequency shifts Δf and Δf_0, which translate to uncertainty in solvent weight fraction of less than 0.0003.

To validate the modifications to the QCM apparatus, we compared the solubilities of benzene in the polyisobutylene polymer measured with the apparatus described here to the results of earlier investigations. Specifically, Figure 2 compares the experimental data for benzene activity versus weight fraction at low solvent concentrations from this modified apparatus to those made previously at higher concentrations both by Iyer et al.[2] and by Wibawa et al.[18] Another way of validating the modified equipment used here is by predicting the benzene activity at low concentrations by using the Flory–Huggins model fit to the higher concentration data for the same system. As seen in Figure 3, the predicted values of weight fraction were found to be within an average of 0.0005. These comparisons show good consistency between the results at lower and higher solvent concentrations.

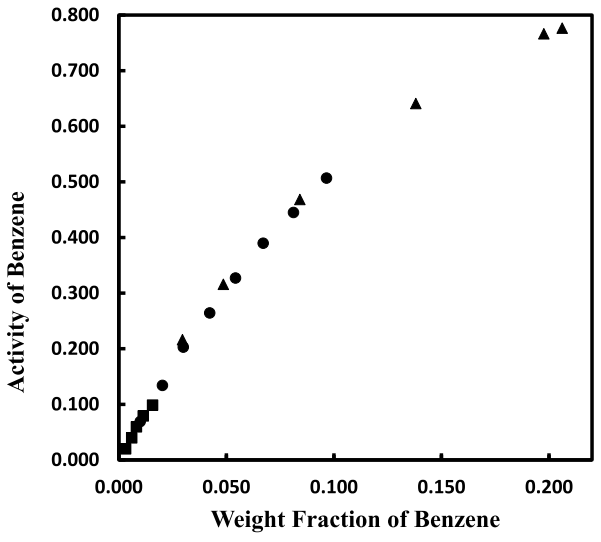

Figure 2. Benzene activity vs benzene weight fraction in PIB for previous apparatus data[2] (●), experimental data from this work (■), and literature data from Wibawa et al.[18] (▲) at 298.15 K.

RESULTS

Previous results[3] from our group have shown the difference between unplasticized and plasticized PEMA films in terms of steep frequency shifts and the amount of time needed for the

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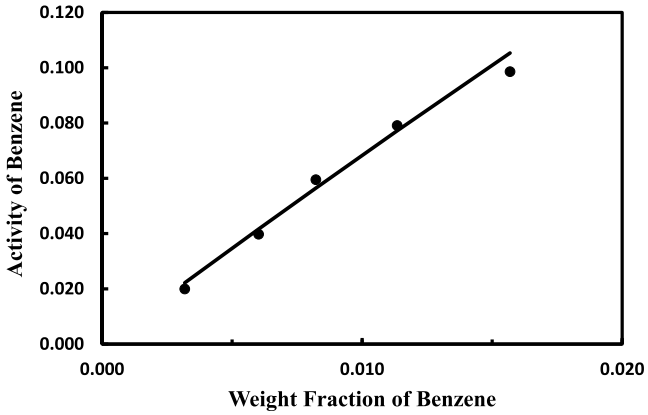

Figure 3. Prediction of benzene activity at lower concentrations by using a Flory–Huggins model fit to higher concentration data from the lab. Benzene activity versus benzene weight fraction in PIB (●); solid curves represent fit to the Flory–Huggins model.

data points to equilibrate. Similar results were seen in this work as well, when 5% of the plasticizer was added to the PEMA film and 15% to the PS film. The systems considered here are denoted as solvent (1) + polymer (2) + plasticizer (3). With plasticizers being nonvolatile, all the data points are for a constant w_3/w_2 ratio, with w_3 being the weight fraction of the plasticizer and w_2 the weight fraction of the polymer. These weight fractions can be recovered from

$$w_3 = (\%\ P)(1 - w_1)/100 \quad (4)$$

$$w_2 = 1 - w_1 - w_3 \quad (5)$$

where % P is either 5 and 15, depending on the film.

Activity versus weight fraction plots for each solvent, namely, benzene, toluene, and ethylbenzene, and polymer–plasticizer films, PEMA–DINCH, PEMA–DIOA, and PS–BS, are shown in Figures 4–6. For a given activity value for benzene, the weight fraction of benzene was the highest in PEMA–DINCH (5%), followed by PEMA–DIOA (5%), and the least in PS–BS (15%), as evident from Figure 4. The reason for higher

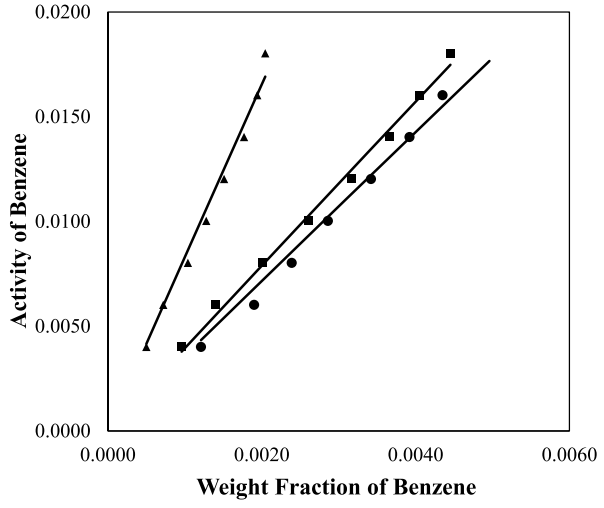

Figure 4. Benzene activity versus benzene weight fraction in DINCH-plasticized PEMA (●), DIOA-plasticized PEMA (■), and BS-plasticized PS (▲) at 298.15 K. Solid curves represent fit to eq 6 to the data.

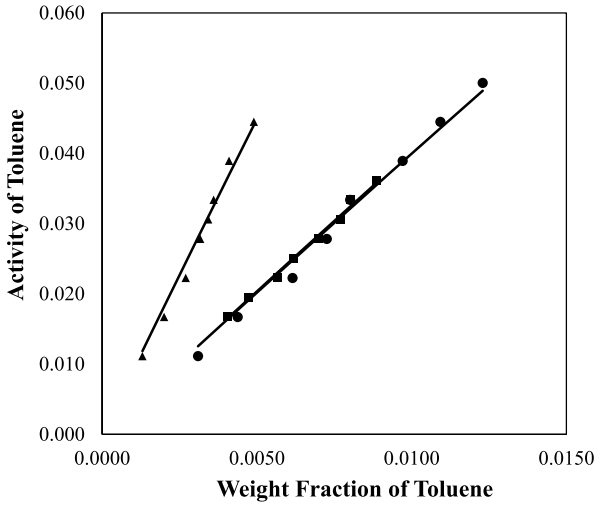

Figure 5. Toluene activity versus toluene weight fraction in DINCH-plasticized PEMA (●), DIOA-plasticized PEMA (■), and BS-plasticized PS (▲) at 298.15 K. Solid curves represent fit to eq 6 to the data.

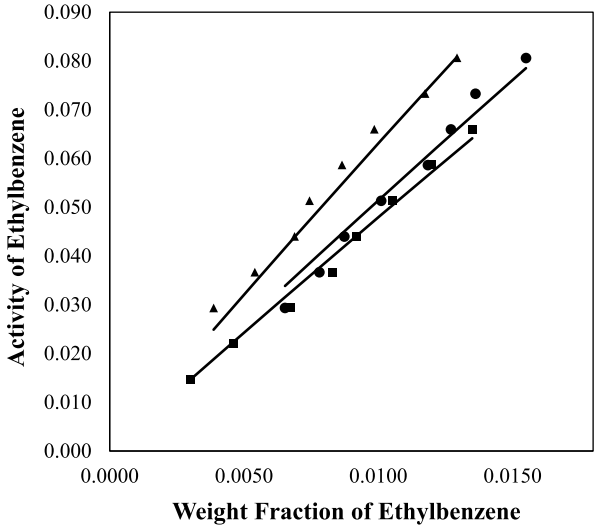

Figure 6. Ethylbenzene activity versus ethylbenzene weight fraction in DINCH-plasticized PEMA (●), DIOA-plasticized PEMA (■), and BS-plasticized PS (▲) at 298.15 K. Solid curves represent fit to eq 6 to the data.

sorption of the analytes in the DINCH-plasticized PEMA film compared to other plasticized films is because of the higher molecular weight of the DINCH plasticizer. The polymer tends to have a greater accessible free volume when a larger-sized molecule has been added compared to a lower-sized molecule, thus enabling higher sorption.[9] This result for higher sorption in DINCH-plasticized PEMA was found to be consistent for the other two solvents, toluene and ethylbenzene, as well. The values for activity versus weight fraction for each solvent and each film are reported in Tables 3–5. There was no literature available for the current use of plasticizer %, but compared to our previous work from Kaur et al.,[3] the experimental data for the DINCH and DIOA films lie between the results for pure PEMA and plasticized PEMA (10%), giving us confidence in the data collected using the newly modified apparatus.

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Table 3. Experimental Weight Fractions w_1 at 298.15 K for Benzene in PEMA−DINCH (5%), PEMA−DIOA (5%), and PS−BS (15%) Films as a Function of Benzene Activity a_1

benzene	PEMA−DINCH (5%)	PEMA−DIOA (5%)	PS−BS (15%)
a_1	w_1	w_1	w_1
0.0040	0.0012	0.0010	0.0005
0.0060	0.0019	0.0014	0.0007
0.0080	0.0024	0.0020	0.0010
0.0100	0.0029	0.0026	0.0013
0.0120	0.0034	0.0032	0.0015
0.0140	0.0039	0.0037	0.0018
0.0160	0.0044	0.0041	0.0019
0.0180	0.0050	0.0045	0.0020

Table 4. Experimental Weight Fractions w_1 at 298.15 K for Toluene in PEMA−DINCH (5%), PEMA−DIOA (5%), and PS−BS (15%) Films as a Function of Toluene Activity a_1

PEMA−DINCH (5%)		PEMA−DIOA (5%)		PS−BS (15%)	
a_1	w_1	a_1	w_1	a_1	w_1
0.011	0.0031	0.017	0.0041	0.0111	0.0013
0.017	0.0044	0.019	0.0047	0.0167	0.0020
0.022	0.0062	0.022	0.0057	0.0223	0.0027
0.028	0.0073	0.025	0.0062	0.0278	0.0032
0.033	0.0080	0.028	0.0070	0.0306	0.0034
0.039	0.0097	0.031	0.0077	0.0334	0.0036
0.044	0.0109	0.033	0.0080	0.0389	0.0041
0.050	0.0123	0.036	0.0088	0.0445	0.0049

Table 5. Experimental Weight Fractions w_1 at 298.15 K for Ethylbenzene in PEMA−DINCH (5%), PEMA−DIOA (5%), and PS−BS (15%) Films as a Function of Ethylbenzene Activity a_1

PEMA−DINCH (5%)		PEMA−DIOA (5%)		PS−BS (15%)	
a_1	w_1	a_1	w_1	a_1	w_1
0.029	0.0065	0.015	0.0030	0.029	0.0039
0.037	0.0078	0.022	0.0046	0.037	0.0054
0.044	0.0087	0.029	0.0068	0.044	0.0069
0.051	0.0101	0.037	0.0083	0.051	0.0074
0.059	0.0118	0.044	0.0092	0.059	0.0087
0.066	0.0127	0.051	0.0105	0.066	0.0099
0.073	0.0136	0.059	0.0120	0.073	0.0117
0.081	0.0155	0.066	0.0140	0.081	0.0129

Data Correlation. It has been shown in our previous work[3] that Flory−Huggins theory for a ternary system consisting of a polymer, plasticizer, and solvent could be simplified. Because the plasticizer/polymer ratio is fixed, these systems can be considered to be pseudo-binary systems with appropriate definitions for the molar volume and molecular weight of the film and the interaction parameter.

By introducing the polymer−plasticizer pseudo-component (f), the solvent activity can be written as

$$\ln a_1 = \ln \phi_1 + (1 - \phi_1)\left(1 - \left(\frac{V_1}{V_f}\right)\right) + \chi_{1f}(1 - \phi_1)^2 \quad (6)$$

where

$$V_f = \frac{\alpha + 1}{\frac{\alpha}{V_3} + \frac{1}{V_2}} \quad (7)$$

$$\chi_{1f} = \chi_{13}\frac{\alpha}{\alpha + 1} + \chi_{12}\frac{1}{\alpha + 1} - \chi_{23}\frac{\alpha}{(\alpha + 1)^2} \quad (8)$$

where a_1, $\emptyset_i$, V_1, V_2, and V_f are the activity of the solvent, the volume fraction of the species, the volume of the solvent, the volume of the polymer, and the volume of the film, respectively, and α is the ratio of volume fractions of the plasticizer over the polymer, given by $\alpha = \emptyset\phi_3/\emptyset_2$. The values of the parameter χ_{1f} are obtained by fitting experimental data to eq 6 and are reported in Table 6.

Table 6. Values of Parameter χ_{1f} in Eq 4 as a Function of $\alpha = \emptyset_3/\emptyset_2$ for the Solvents Benzene, Toluene, and Ethylbenzene in Plasticized PEMA and PS Films

solvent	film	α	χ_{1f}
benzene	PEMA−DINCH	0.061	0.062
toluene	PEMA−DINCH	0.061	0.184
ethylbenzene	PEMA−DINCH	0.061	0.439
benzene	PEMA−DIOA	0.064	0.162
toluene	PEMA−DIOA	0.064	0.195
ethylbenzene	PEMA−DIOA	0.064	0.37
benzene	PS−BS	0.230	0.970
toluene	PS−BS	0.230	1.061
ethylbenzene	PS−BS	0.230	0.760

Infinite dilution partition coefficients (K^∞) may be calculated from

$$K^\infty = \left[\frac{\rho_f RT}{\Omega^\infty M_1 P_1^{sat}}\right] \quad (9)$$

where ρ_f is the density of the film, R is the gas constant, T is the temperature of the cell, M_1 is the molecular weight of the solvent, $P1$sat is the saturated vapor pressure of the solvent, and Ω^∞ is the weight-based infinite dilution activity coefficient, which can be obtained from the pseudo-binary Flory−Huggins model via

$$\ln \Omega^\infty = \ln\left(\frac{V_1}{V_f} * \frac{M_f}{M_1}\right) + 1 - \frac{V_1}{V_f} + \chi_{1f} \quad (10)$$

where, V_1, V_f, M_1, and M_f are the volume and molecular weight of the solvent and film, respectively, and χ_{1f} is the value obtained by fitting the experimental data to eq 6. M_f, which is the molecular weight of the film, is given by

$$M_f = \frac{V_3 M_2 + \alpha V_2 M_3}{V_3 + \alpha V_2} \quad (11)$$

where V_2, V_3, M_2, and M_3 are the molecular weights and volumes of the polymer and plasticizer, respectively. The values of infinite dilution partition coefficients so obtained are given in Table 7. It could be seen that for both benzene and toluene, the infinite dilution partition coefficients in the plasticized PEMA polymer are greater than those in pure PEMA. Data for pure PS could not be measured as the polymer is glassy under these experimental conditions.

CONCLUSIONS

Solubilities of benzene, toluene, and ethylbenzene in plasticized PEMA and PS at 298.15 K are reported in the form of activity versus weight fraction data. It is observed that for a given activity, the sorption of the solvents was maximum

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Table 7. Values of Infinite Dilution Partition Coefficients (K^{∞}) for the Solvents Benzene, Toluene, and Ethylbenzene in Pure PEMA, Plasticized PEMA, and PS Films

film	benzene K^{∞}	toluene K^{∞}	ethylbenzene K^{∞}
pure PEMA	623	1423	4035
PEMA−DINCH	766	1908	3899
PEMA−DIOA	693	1887	4181
pure PS			
PS−BS	318	817	2945

in the PEMA−DINCH film, followed by PEMA−DIOA, and the least in the PS−BS film because of the plasticizer structure and molecular weight. The experimental data were interpreted using the pseudo-binary Flory−Huggins model. It was found that sorption is enhanced in plasticized polymer films compared to unplasticized polymer films as evident in both sorption data and infinite dilution partition coefficient values.

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Notes

The authors declare no competing financial interest.

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