Solubilities of Dichloromethane, Diethyl Ether, Ethyl Acetate, and Nitrobenzene in Three Polymers Using the Piezoelectric Quartz Sorption Method

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The solubilities of dichloromethane, diethyl ether, ethyl acetate, nitrobenzene in polyisobutylene (PIB), poly(*n*-butyl methacrylate) (PBMA), and poly(vinyl acetate) (PVAc) were measured by the piezoelectric quartz crystal microbalance method at four temperatures, (293.2, 313.2, 333.2, and 353.2) K. In this work, three quartz crystals were installed in an equilibrium cell, which enables multiple solubility measurements. The estimated experimental uncertainty was less than 1 % for solvent activity and 6.6 % mass fraction at the lowest solubility region, with a lower uncertainty being found in the higher solubility region. The accuracy of the apparatus was confirmed by comparison of the experimental data obtained in this work with the literature data. The Flory−Huggins equation with the temperature-dependent interaction parameter was used for the correlation of the experimental data with an overall average absolute deviation in activities of 6.5 %.

Introduction

The production of polymers in the world has been continuously rising over the last 20 years.[1] The increasing demands for higher polymer quality lead the development of new techniques for polymer finishing processing. One of the major goals in polymer processing is the efficient removal or recycling of unpolymerized monomers and polymerization solvent from polymer products as required to meet environment, health, and safety regulations. Therefore, vapor−liquid equilibria (VLE) data of solvent + polymer systems is necessary in several industrial sectors such as surface acoustic-wave sensors,[2,3] the recovery of organic vapors from waste-air streams using a polymeric membrane,[4,5] pervaporation,[6] polymer devolatilization,[7] vapor-phase photografting,[8] and the formulation of paints and coatings.[9] These data also serve a fundamental basis for studying intermolecular interactions and developments of thermodynamic models.

VLE data for some polymer solutions have been compiled in some references.[10−13] However, the database for polymer solutions is limited in the number of systems and in the experimental conditions available. Several experimental techniques have been employed to measure the solvent activities of polymer solution such as gas chromatography,[14−17] gravimetric sorption,[18−20] and a piezoelectric sorption detector.[21−31]

The detector, which is known as a piezoelectric quartz crystal microbalance (QCM), is well-known in the field of thin-film monitoring[32] and has been used as chemical sensors[33,34] to monitor the absorption of gases and vapors by crystals covered with functionalized coatings. The principle of the method is based on the linear relationship between frequency shift and mass shift at the surface of the crystal as first described by Sauerbrey.[35] Many researchers have reported the application of this method to measure the solubility of organic vapors and high-pressure gases in polymers.[21−23] The method offers the advantageous of high sensitivity since it uses small amounts of polymer spread in a thin film and generating data much more rapidly than alternative gravimetric methods.[28]

In our previous paper,[29,30] we studied the reliability of the QCM method to generate the solubility of both polar and nonpolar solvents in polymers. In this present work, we applied the method to determine experimentally the solubility of dichloromethane, diethyl ether, ethyl acetate, and nitrobenzene in polyisobutylene (PIB), poly(*n*-butyl methacrylate) (PBMA), and poly(vinyl acetate) (PVAc) at the temperatures of (293.2, 313.2, 333.2, and 353.2) K, respectively. The experimental solvent activity data for all systems were correlated using the Flory−Huggins equation.[36]

Table 1. Characteristics of Polymers Used

polymer	T_g[a] / K	T_m[a] / K	10^{-3} M_w[b] / g·mol^{-1}
PIB	197.2	274.7	500
PBMA	288.2	-	337
PVAc	303.2	-	167

[a] T_g = glass transition temperature; T_m = melting temperature (supplier specification). [b] M_w = weight average molecular mass (supplier specification).

Experimental Section

Materials. Dichloromethane ($w > 0.999$), diethyl ether ($w > 0.99$), ethyl acetate ($w > 0.99$), and nitrobenzene ($w > 0.99$) were purchased from the Merck, Germany. The three amorphous polymers used for each measurement in this work were PIB, PBMA, and PVAc purchased from the Aldrich Chemical Co. (USA) with characteristics shown in Table 1. All of the purchased materials were used without further purification.

Apparatus. Figure 1 presents the QCM apparatus used for these measurements which is essentially similar to the previous experiments.[29,30] It consists of sorption cell, solvent tank, frequency measuring section, and vacuum section. Three quartz-crystal sensors with a base frequency of 5 MHz, AT-cut type, 5.5 mm diameter, and 0.3 mm thickness were installed in the equilibrium cell to determine the amount of solvent absorbed

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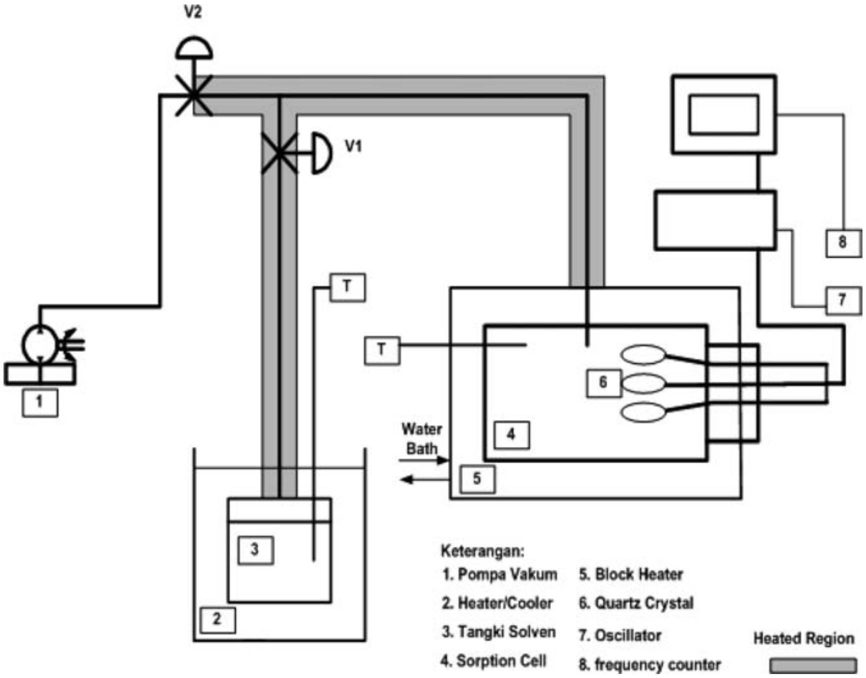

Figure 1. Schematic diagram of quartz crystal microbalance method.

in the polymer sample under equilibrium temperature and pressure. The installed crystals enabled the simultaneous solubility measurements of solvent vapor in three different polymers. The temperatures of the sorption cell and the solvent tank were measured by four-wire platinum resistance temperature detectors and were recorded by a digital temperature indicator (Yokogawa 7563) with an accuracy of ± 0.03 K. The temperature detectors and the temperature indicator were calibrated against a standard thermometer (Kays X0860) with an accuracy of ± 0.01 K. Tape heaters were used to ensure that no solvent vapor condensed on the line from the solvent tank to the sorption cell and was set (5 to 10) K higher than the cell temperature. Two water baths were installed for separately controlling temperatures in the sorption cell and in the solvent tank within ± 0.02 K.

Solubility Measurements. The solubility measurements were carried out at (293.2, 313.2, 333.2, and 353.2) K. The detailed procedure used in this work has been described in our earlier work.[29] Briefly, each of the polymers used in this work was dissolved in toluene at 353.2 K to make a solution of 1 % mass fraction of polymer for the preparation of polymer coating. One drop of the solution then coated on both surfaces of clean crystal sensor with desired film thickness corresponds to the frequency shift due to polymer coating around 3000 Hz. After three crystals have been coated with different polymer solutions, crystals were allowed to dry at ambient conditions, and afterward the crystals were set in the cell. Volatile low molecular substances and impurities including air inside the cell were evacuated from the cell using a vacuum pump. Then the vapor of one of the solvents was introduced into the cell from the solvent tank. After equilibrium conditions and a stable frequency value within an acceptable tolerance (± 5 Hz) had been reached, the reading was recorded as an equilibrium value. The frequency shifts resulting from coated polymer and vapor sorption were denoted as Δf_0 and Δf_1, respectively. Experimental uncertainties in the solvent activity were based on frequency fluctuations and temperature measurements for both the solvent tank and the sorption cell, which were ± 5 Hz and ± 0.05 K, respectively.

Using the Sauerbrey's equation,[35] the mass fraction of solvent, w_1, absorbed by the polymer can be calculated by the measurement of the frequency shift by the following equation:

$$w_1 = \frac{\Delta f_1}{\Delta f_0 + \Delta f_1} \tag{1}$$

Solvent activities were calculated indirectly from vapor and liquid phase properties for each sorption data point. The derivation can be started from isofugacity criteria by equating the solvent fugacities in the vapor and the liquid phases when the system reached the equilibrium condition:

$$f_1^{\mathrm{vap}} = f_1^{\mathrm{liq}} \tag{2}$$

By assuming that polymer is nonvolatile and the vapor phase to be pure solvent, the solvent fugacity in the solvent vapor phase, f_1^{vap}, can be found from the product solvent partial pressure, P_1, and the fugacity coefficient, ϕ_1:

$$f_1^{\mathrm{vap}} = \phi_1 P_1 \tag{3}$$

and by ignoring the Poynting factor, the solvent fugacity in the liquid phase, f_1^{liq}, is found from the product of solvent activity, a_1, the solvent vapor pressure, P_1^{S}, and the fugacity coefficient in saturated condition, ϕ_1^{S}:

$$f_1^{\mathrm{liq}} = a_1 P_1^{\mathrm{S}} \phi_1^{\mathrm{S}} \tag{4}$$

Since the experiment was conducted at a moderate pressure, the fugacity coefficient can be estimated through use of second virial coefficient, B_1:

$$\phi_1 = \exp\left(\frac{B_1 P_1}{RT}\right) \qquad \phi_1^{\mathrm{S}} = \exp\left(\frac{B_1 P_1^{\mathrm{S}}}{RT}\right) \tag{5}$$

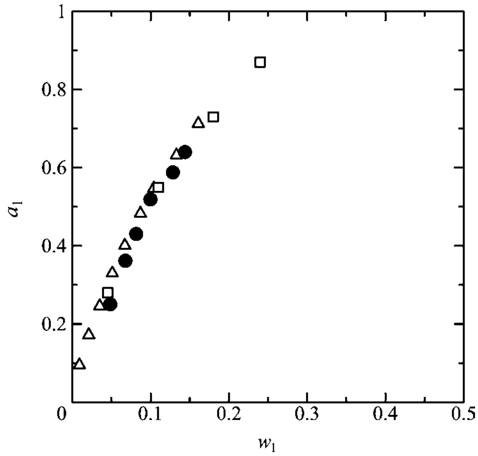

Figure 2. Activities of toluene a_1 in toluene (1) + PVAC (2) at mass fraction w_1 and comparison with literature values at $T = 333.2$ K: ●, this work; △, ref 29; and □, ref 39.

Combining eqs 2, 3, 4, and 5, the solvent activity will have the form as:

$$a_1 = \frac{P_1}{P_1^S} \exp\left(\frac{-B_1(P_1^S - P_1)}{RT}\right) \qquad (6)$$

where B_1 can be calculated from the correlation of Tsonopoulos.[37] P_1 is the equilibrium pressure, which is equal to the vapor pressure of the solvent at the temperature of the solvent tank. P_1^S is evaluated at temperature of the sorption cell, T, and calculated using the Wagner equation, with constants given by Poling et al.,[38] while R is the gas constant.

Results and Discussion

The experimental uncertainty of solvent activity in this work was estimated to be less than 1 % based on uncertainty in temperature measurements for both the solvent tank and the sorption cell within ± 0.05 K and the Tsonopolous correlation.[37] The experimental uncertainty of the mass fraction of solvent raised from fluctuations in the frequency at equilibrium within ± 5 Hz was a maximum of 6.6 % for the lowest solubility region, and a lower uncertainty was found for higher solubility region.

To verify the present experimental apparatus for the solubility measurements, our experimental data for the system of toluene + PVAc are compared with those of published data at a temperature of 333.2 K as shown in Figure 2. Good agreement can be observed with the published data,[29,39] especially in the higher solubility region. However, the reported solubility measurements for this system in the range of the lower solubility region exhibited a discrepancy with literature values which is likely due to systematic error arising during measurements and the different weight molecular masses of PVAc used by a previous investigator.[39] For this system, the authors reported solubility data with an weight average molecular mass of polymer of 230 000 g·mol^{-1} by using the quartz spring sorption balance technique. The difference can be expected to exhibit molecular mass dependence.

Table 2. Mass Fraction w_1 and Activities of Dichloromethane a_1 in PIB, PBMA, and PVAc

PIB		PBMA		PVAc	
a_1	w_1	a_1	w_1	a_1	w_1
		T/K = 293.2			
0.324	0.047	0.556	0.095	-	-
0.408	0.058	0.636	0.133	-	-
0.624	0.108	0.681	0.144	-	-
0.711	0.121	0.726	0.166	-	-
-	-	0.831	0.208	-	-
		T/K = 313.2			
0.191	0.039	0.184	0.040	0.325	0.079
0.243	0.053	0.264	0.065	0.364	0.091
0.303	0.064	0.291	0.068	0.412	0.108
0.409	0.086	0.310	0.074	0.459	0.124
0.463	0.095	0.347	0.083	0.489	0.133
-	-	0.393	0.094	-	-
-	-	0.455	0.117	-	-
		T/K = 333.2			
0.190	0.060	0.192	0.084	0.224	0.064
0.223	0.072	0.213	0.092	0.286	0.081
0.257	0.083	0.241	0.101	0.292	0.083
0.279	0.091	0.263	0.110	0.344	0.102
0.311	0.103	-	-	0.406	0.122
-	-	-	-	0.458	0.142
		T/K = 353.2			
0.256	0.134	0.056	0.061	0.192	0.109
0.289	0.146	0.076	0.072	0.227	0.121
0.325	0.161	0.081	0.080	0.266	0.138
0.350	0.185	0.099	0.090	0.310	0.159
0.380	0.194	0.108	0.098	0.362	0.188

Table 3. Mass Fraction w_1 and Activities of Ethyl Acetate a_1 in PIB, PBMA, and PVAc

PIB		PBMA		PVAc	
a_1	w_1	a_1	w_1	a_1	w_1
		T/K = 293.2			
0.376	0.024	0.376	0.047	-	-
0.455	0.029	0.455	0.065	-	-
0.584	0.034	0.665	0.088	-	-
0.766	0.049	0.766	0.122	-	-
		T/K = 313.2			
0.131	0.013	0.162	0.023	0.273	0.067
0.265	0.026	0.197	0.032	0.320	0.083
0.480	0.040	0.232	0.047	0.480	0.119
0.690	0.065	0.581	0.127	0.583	0.185
		T/K = 333.2			
0.339	0.036	0.305	0.079	0.154	0.032
0.450	0.045	0.397	0.104	0.198	0.044
0.555	0.064	0.504	0.147	0.305	0.114
0.670	0.077	0.617	0.241	0.450	0.157
		T/K = 353.2			
0.300	0.032	0.117	0.035	0.143	0.032
0.343	0.040	0.212	0.058	0.179	0.071
0.458	0.056	0.245	0.096	0.212	0.136
0.590	0.082	0.300	0.133	0.300	0.165
0.645	0.095	0.458	0.245	0.343	0.182
-	-	-	-	0.379	0.206

Twelve sets of experimental solubility data of solvent + polymer systems at temperatures of (293.2, 313.2, 333.2, and 353.2) K obtained in this work were presented through Tables 2 to 5. All measurements were made at the temperature above the glass temperature of the polymer. The solubility measurements for systems containing poly(vinyl acetate) at temperatures of 293.2 K could not been carried out since the equilibrium temperature is lower than the glass temperature.

For all of the systems studied, the solubility of solvent in polymer increases with increasing temperature as represented in Figure 3 for the dichloromethane + PIB system and Figure 4 for the ethyl acetate + PBMA system.

Polar solvents (dicholomethane, diethyl ether, and ethy acetate) studied tend to show the low solubilities in PIB and

Table 4. Mass Fraction w_1 and Activities of Diethyl Ether a_1 in PIB, PBMA, and PVAc

PIB		PBMA		PVAc	
a_1	w_1	a_1	w_1	a_1	w_1
		T/K = 293.2			
0.581	0.101	0.652	0.138	-	-
0.625	0.114	0.726	0.164	-	-
0.633	0.119	0.765	0.177	-	-
0.695	0.128	0.828	0.203	-	-
		T/K = 313.2			
0.348	0.085	0.312	0.098	0.383	0.130
0.383	0.096	0.348	0.112	0.426	0.142
0.426	0.112	0.383	0.124	0.475	0.158
0.642	0.184	0.426	0.134	0.535	0.182
		T/K = 333.2			
0.317	0.097	0.321	0.112	0.317	0.128
0.341	0.106	0.348	0.122	0.341	0.140
0.405	0.121	0.373	0.131	0.405	0.154
0.472	0.140	0.395	0.141	0.533	0.211
		T/K = 353.2			
0.364	0.130	0.229	0.125	0.359	0.168
0.429	0.150	0.259	0.135	0.416	0.198
0.465	0.163	0.288	0.143	0.458	0.216
0.502	0.199	0.364	0.177	0.507	0.250
-	-	-	-	0.643	0.285

Table 5. Mass Fraction w_1 and Activities of Nitrobenzene a_1 in PIB, PBMA, and PVAc

PIB		PBMA		PVAc	
a_1	w_1	a_1	w_1	a_1	w_1
		T/K = 293.2			
0.212	0.029	0.171	0.028	-	-
0.248	0.036	0.224	0.040	-	-
0.261	0.040	0.261	0.049	-	-
0.322	0.047	0.365	0.069	-	-
0.365	0.053	-	-	-	-
		T/K = 313.2			
0.037	0.008	0.036	0.010	0.062	0.010
0.048	0.011	0.062	0.018	0.097	0.015
0.062	0.014	0.097	0.029	0.193	0.034
0.087	0.020	0.136	0.040	0.290	0.052
0.290	0.073	-	-	-	-
		T/K = 333.2			
0.322	0.105	0.147	0.050	0.188	0.041
0.389	0.132	0.188	0.062	0.238	0.051
0.437	0.150	0.433	0.155	0.342	0.078
0.506	0.199	0.480	0.162	0.433	0.100
				0.553	0.143
		T/K = 353.2			
0.177	0.064	0.051	0.032	0.087	0.019
0.225	0.088	0.087	0.051	0.225	0.055
0.367	0.138	0.164	0.088	0.306	0.078
0.458	0.191	0.231	0.117	0.366	0.093
-	-	-	-	0.458	0.133

PBMA. Figure 5 shows the solubility of ethyl actetate in three polymers at 353.2 K. As presented in the figure, the solubility values are found to be lowest in nonpolar polymers (PIB). However, the solubility of nitrobenzene (nonpolar solvent) was found to be lowest in strong polar polymer (PVAc) as shown in Figure 6.

The experimental data obtained in this work were correlated with the Flory−Huggins equation:

$$\ln a_1 = \ln(1 - \phi_2) + \phi_2 + \chi\phi_2^{\,2} \tag{7}$$

where ϕ_2 is the volume fraction of the polymer. For each system, this equation contains one interaction parameter, χ_{12}, defined by the linear function of temperature:

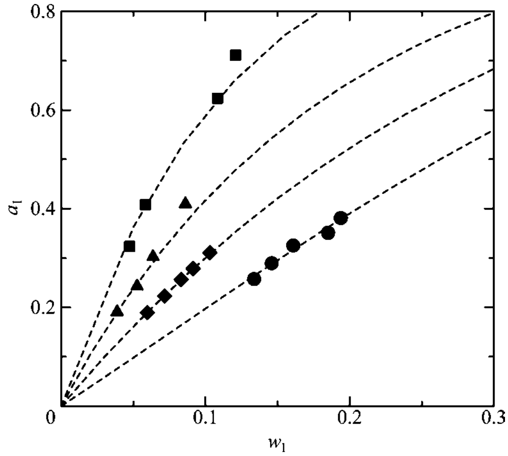

Figure 3. Activities of dicholomethane, a_1, in dicholomethane (1) + PIB (2) at various temperatures: ■, T = 298.2 K; ▲, T = 313.2 K; ◆, T = 333.2 K; ●, T = 353.2 K; and ---, Flory−Huggins equation.

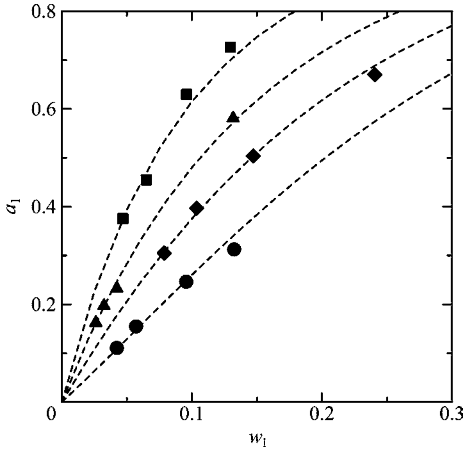

Figure 4. Activities of ethyl acetate a_1 in ethyl acetate (1) + PBMA (2) at various temperatures: ■, T = 293.2 K; ▲, T = 313.2 K; ◆, T = 333.2 K; ●, T = 353.2 K; and ---, Flory−Huggins equation.

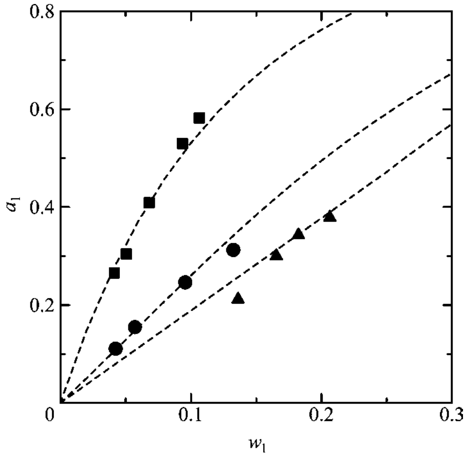

Figure 5. Activities of ethyl acetate a_1 at T = 353.2 K in: ■, ethyl acetate (1) + PIB(2); ●, ethyl acetate (1) + PBMA(2); ▲, ethyl acetate (1) + PVAC (2); and ---, Flory−Huggins equation.

$$\chi_{ij} = k_{ij} + l_{ij}T \tag{8}$$

where k_{ij} and l_{ij} are temperature-independent constants fitted by the experimental data. The best fit for the Flory−Huggins parameters is presented in Table 6 along with the percent absolute average deviations (% AAD) of the solvent activity obtained from the experiment and calculated ones. The independent temperature interaction parameter for the Flory−Huggins

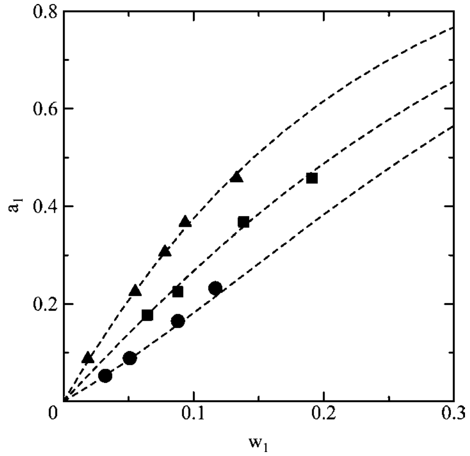

Figure 6. Activities of nitrobenzene a_1 at $T = 353.2$ in: ■, nitrobenzene (1) + PIB (2); ●, nitrobenzene (1) + PBMA (2); ▲, nitrobenzene (1) + PVAC (2); and ---, Flory−Huggins equation.

Table 6. Independent Temperature Interaction Parameters for the Flory−Huggins Equation Fitted in This Work and Average Absolute Deviation (AAD) between Measured and Calculated Solvent Activities

solvent	polymer	T/K[a]	k_{12}	l_{12}	AAD[b]/%
dichloromethane	PIB	293.2−353.2	8.1457	−0.0255	3.7
	PBMA	293.2−353.2	12.139	−0.0394	10.0
	PVAc	313.2−353.2	8.9883	−0.0289	9.9
diethyl ether	PIB	293.2−353.2	6.1602	−0.021	5.6
	PBMA	293.2−353.2	9.5015	−0.0332	7.6
	PVAc	313.2−353.2	7.8054	−0.0296	2.6
ethyl acetate	PIB	293.2−353.2	5.2811	−0.0146	7.5
	PBMA	293.2−353.2	7.1744	−0.0232	4.0
	PVAc	313.2−353.2	13.865	−0.0457	7.9
nitrobenzene	PIB	293.2−353.2	5.3709	−0.0173	7.9
	PBMA	293.2−353.2	6.3119	−0.0215	8.9
	PVAc	313.2−353.2	2.8126	−0.0092	2.8
overall					6.5

[a] Temperature range. [b] AAD = $(100/\mathrm{NP})|(a_1^{\mathrm{calcd}} - a_1^{\mathrm{expt}})/a_1^{\mathrm{expt}}|$; NP = number of data points; superscripts calcd and expt denote the calculated and experimental values.

equation obtained in this work is expected to be convenient in engineering practice, since they allow solubility calculations at various temperatures using one set of parameters.

Conclusions

Solubility data of 12 sets of systems containing organic solvents (dichloromethane, diethyl ether, ethyl acetate, and nitrobenzene) and polymers PIB, PBMA, and PVAc have been measured at temperatures of (293.2, 313.2, 333.2, and 353.2) K using the piezoelectric quartz crystal method. The solubility of dichloromethane, diethyl ether, and ethyl acetate was found to be low in nonpolar and slight polar polymers (PIB and PBMA), and the solubility of nitrobenzene was found to be lowest in strong polar polymer (PVAc). For all systems studied, the solubility increases with increasing the temperature. The experimental data were correlated using the Flory−Huggins activity equation using temperature-independent interaction parameters with an overall AAD of 6.5 %.

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