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Solubility of Seven Nonpolar Organic Solvents in Four Polymers Using the Piezoelectric−Quartz Sorption Method

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Solubility of octane, cyclopentane, cyclohexane, benzene, toluene, ethylbenzene and *p*-xylene in *cis*-1,4-polyisoprene, polyisobutylene, poly(*n*-butyl methacrylate), and poly(vinyl acetate) 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, four quartz crystals were installed in an equilibrium cell, which enables multiple solubility measurements. Estimated uncertainties of measured variables were ±0.05 K for temperature, ±0.009 for activity, and ±0.002 for mass fraction. The accuracy of the method was confirmed by comparison with literature data. The activities obtained were correlated by the UNIQUAC equation with an overall AAD of 4.1%.

Introduction

The solubility of vapors of low molecular weight substances in polymers is important in the design and operation of polymer plants. The removal of residual monomers, oligomers, and polymerization solvents from the produced polymers requires this knowledge. While vapor−liquid equilibria and solubility data have been measured for many years and are available in the literature,[1,2] the data are limited in the number of systems and in the experimental conditions available.

The application of quartz crystal microbalance (QCM) devices for sensing chemical vapor was first described by King[3] and has remained an active research field. This technique has been applied by many researchers[4−11] for the solubility measurement of organic vapors and high-pressure gases in polymers. The method has high sensitivity and offers the advantageous of generating data much more rapidly than alternative gravimetric methods such as electronic and quartz spring microbalances as shown by Mikkilineni et al.,[11] French and Koplos,[12] and Boudouris et al.[13]

In this study, a piezoelectric quartz crystal microbalance apparatus was used to determine the solubility of seven organic solvents (octane, cyclopentane, cyclohexane, benzene, toluene, ethylbenzene, and *p*-xylene) in *cis*-1,4-polyisoprene, polyisobutylene, poly(*n*-butyl methacrylate), and poly(vinyl acetate) at (293.2, 313.2, 333.2, and 353.2) K.

Experimental Section

Principle of QCM Method. The relationship between the change in mass of the crystal, Δm, and the resonance frequency shift, Δf, is expressed by Sauerbrey[14] as

$$\Delta f = -C\Delta m \tag{1}$$

where C is the constant encompassing physical and geometrical properties of the crystal. The above equation is applied to the two cases of polymer coating (frequency shift, Δf_0, due to the mass of polymer film, Δm_0) and dissolved solvent in polymer (frequency shift, Δf_1, due to the mass of dissolved solvent, Δm_1). The mass fraction of the solvent dissolved in the polymer, w_1, is obtained by the measurement of frequency shifts as shown in the following equation:

$$w_1 = \frac{\Delta m_1}{\Delta m_0 + \Delta m_1} = \frac{\Delta f_1}{\Delta f_0 + \Delta f_1} \tag{2}$$

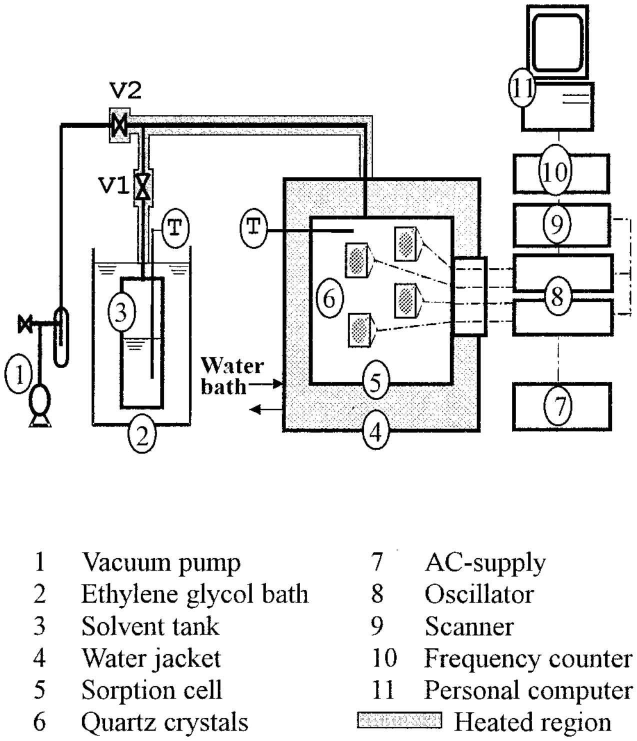

Figure 1. Schematic diagram of piezoelectric sorption apparatus.

Apparatus. The experimental apparatus is shown schematically in Figure 1. It consists of four sections: a sorption cell, a solvent tank, a frequency measuring section, and a

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Table 1. Characteristics of Polymers Used

polymer	T_g/K^a	T_m/K^a	$10^{-3}M_w$/g·mol$^{-1\,b}$
PI	202.2	309.2	800
PIB	197.2	274.7	500
PBMA	288.2		337
PVAc	303.2		167

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

Table 2. Solubility of Octane in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc)

PI		PIB		PBMA		PVAc	
a_1	w_1	a_1	w_1	a_1	w_1	a_1	w_1
(T = 293.2 K)		(T = 293.2 K)		(T = 293.2 K)		(T = 313.2 K)	
0.330	0.058	0.327	0.066	0.261	0.028	0.179	0.001
0.420	0.079	0.422	0.093	0.332	0.039	0.260	0.001
0.495	0.099	0.492	0.113	0.420	0.053	0.328	0.002
0.565	0.120	0.565	0.140	0.497	0.066	0.413	0.002
0.642	0.144	0.634	0.171	0.563	0.079	0.495	0.003
0.731	0.175	0.724	0.217	0.638	0.095	0.567	0.004
0.800	0.197	(T = 313.2 K)		0.724	0.118	0.655	0.005
(T = 313.2 K)		0.174	0.035	0.804	0.152	0.722	0.006
0.174	0.032	0.254	0.054	(T = 313.2 K)		0.809	0.007
0.254	0.049	0.324	0.072	0.100	0.012	(T = 333.2 K)	
0.324	0.064	0.408	0.098	0.179	0.023	0.102	0.001
0.408	0.083	0.493	0.130	0.261	0.034	0.179	0.003
0.493	0.105	0.557	0.156	0.328	0.046	0.260	0.005
0.557	0.123	(T = 333.2 K)		0.413	0.061	0.336	0.006
0.638	0.147	0.102	0.021	0.495	0.078	0.414	0.008
0.709	0.168	0.179	0.037	0.567	0.095	0.489	0.009
(T = 333.2 K)		0.260	0.057	0.655	0.120	0.565	0.011
0.100	0.016	0.336	0.077	0.722	0.144	0.645	0.014
0.180	0.031	0.414	0.099	0.809	0.180	0.738	0.018
0.255	0.045	0.489	0.119	(T = 333.2 K)		0.810	0.022
0.327	0.059	0.565	0.136	0.102	0.013	(T=353.2 K)	
0.401	0.075	0.645	0.151	0.179	0.024	0.098	0.002
0.484	0.094	(T=353.2 K)		0.260	0.038	0.175	0.004
0.556	0.111	0.099	0.024	0.336	0.050	0.252	0.007
0.640	0.132	0.174	0.044	0.414	0.066	0.332	0.009
0.720	0.152	0.261	0.065	0.489	0.083	0.406	0.011
(T = 353.2 K)		0.330	0.078	0.565	0.103	0.483	0.014
0.099	0.017			0.645	0.129	0.563	0.017
0.174	0.031			0.738	0.166		
0.261	0.048			0.810	0.214		
0.330	0.061			(T = 353.2 K)			
0.405	0.076			0.098	0.013		
0.482	0.095			0.175	0.024		
0.559	0.111			0.252	0.037		
0.635	0.124			0.332	0.052		
				0.406	0.069		
				0.483	0.089		
				0.563	0.116		
				0.646	0.152		
				0.731	0.184		

Table 3. Solubility of Cyclopentane in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc)

PI		PIB		PBMA		PVAc	
a_1	w_1	a_1	w_1	a_1	w_1	a_1	w_1
(T = 293.2 K)		(T = 293.2 K)		(T = 293.2 K)		(T = 313.2 K)	
0.346	0.090	0.346	0.083	0.346	0.061	0.194	0.002
0.394	0.100	0.394	0.097	0.394	0.072	0.259	0.003
0.449	0.106	0.449	0.116	0.449	0.086	0.337	0.006
(T = 313.2K)		0.498	0.135	0.498	0.099	0.414	0.009
0.194	0.033	0.558	0.163	0.558	0.117	0.484	0.013
0.259	0.038	0.611	0.187	0.611	0.136	0.573	0.018
(T = 333.2 K)		(T = 313.2 K)		0.712	0.179	0.638	0.023
0.095	0.013	0.194	0.045	0.758	0.202	0.712	0.030
0.172	0.018	0.259	0.064	0.822	0.247	0.801	0.040
0.250	0.027	0.337	0.090	(T = 313.2 K)		(T = 333.2 K)	
0.326	0.034	0.414	0.117	0.194	0.034	0.096	0.004
		0.484	0.134	0.259	0.048	0.171	0.007
		(T = 333.2 K)		0.337	0.066	0.250	0.012
		0.096	0.026	0.414	0.086	0.324	0.018
		0.171	0.047	0.484	0.108	0.398	0.024
		0.250	0.067	0.573	0.141	0.479	0.031
		0.324	0.078	0.638	0.168	0.561	0.040
		(T = 353.2 K)		0.712	0.214	0.633	0.048
		0.094	0.002	0.801	0.296	0.711	0.059
				(T = 333.2 K)		0.797	0.072
				0.103	0.018	(T = 353.2 K)	
				0.177	0.034	0.098	0.006
				0.256	0.052	0.174	0.012
				0.330	0.071	0.252	0.018
				0.405	0.091	0.328	0.025
				0.485	0.118	0.396	0.031
				0.566	0.152	0.476	0.040
				0.638	0.197	0.553	0.049
				0.716	0.238	0.632	0.060
				(T = 353.2 K)		0.706	0.072
				0.098	0.020		
				0.174	0.038		
				0.252	0.059		
				0.328	0.082		
				0.396	0.108		
				0.476	0.148		

vacuum section. Water and ethylene glycol baths were installed for separately controlling temperatures in the sorption cell and in the solvent tank within ±0.02 K. 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 accuracy of ±0.03 K. The temperature detectors and the temperature indicator were calibrated against a standard thermometer (KAYS, X0860, with accuracy of ±0.01 K). The sorption cell contains four quartz crystals, which enables the simultaneous solubility measurements of a solvent vapor in four different polymers. To prevent solvent vapor from condensing, the temperature of the line from the solvent tank to the sorption cell was set (5 to 10) K higher than the cell temperature by heating with tape heaters along the line. The quartz crystal microbalance sensors used in the present experiment were 5 MHz, AT-cut, 5.5 mm in diameter, and 0.3 mm thick.

Method for Polymer Coating. Both surfaces of each microbalance sensor were coated with polymers by the following procedure. A polymer + toluene solution of 1 mass % was prepared at 80 °C. One drop of the solution was placed on the clean crystal surface, which was supported horizontally and was allowed to dry at room temperature. This procedure was repeated for both sides of the crystal until a desired thickness of the film (0.3 to 0.8) μm corresponding to frequency shift due to polymer coating, Δf_0= (3000 to 8000) Hz was reached as recommended in the previous work.[5,6]

Experimental Procedure and Data Reduction. Frequencies of the clean crystals were determined first at the desired temperature. After all of the crystals were coated with polymers and the crystals were set in the cell, volatile low molecular substances and impurities including air were evacuated from the cell and frequencies of the coated crystals were recorded. Then the vapor of one of the solvents was introduced into the cell from the solvent tank. The frequency of each crystal was scanned and was recorded as a function of time by a personal computer. When it reached a stable value within an acceptable tolerance (±5 Hz), 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.

Table 4. Solubility of Cyclohexane in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc)

		w_1			
T/K	a_1	PI	PIB	PBMA	PVAc
293.2	0.513	0.139	0.143	0.092	
	0.558	0.158	0.161	0.104	
	0.593	0.173	0.176	0.113	
	0.626	0.176	0.192	0.122	
	0.655	0.200	0.208	0.133	
	0.692	0.217	0.231	0.146	
	0.732	0.237	0.260	0.162	
	0.765	0.254	0.287	0.177	
	0.783	0.263	0.301	0.185	
313.2	0.329	0.081	0.086	0.059	0.015
	0.405	0.105	0.112	0.076	0.020
	0.482	0.130	0.144	0.096	0.025
	0.561	0.158	0.182	0.120	0.030
	0.636	0.186	0.222	0.148	0.035
	0.705	0.211	0.241	0.178	0.043
	0.790			0.231	0.055
333.2	0.175	0.040	0.045	0.030	0.010
	0.252	0.060	0.068	0.046	0.016
	0.328	0.081	0.094	0.063	0.022
	0.402	0.103	0.122	0.082	0.029
	0.485	0.127	0.154	0.105	0.036
	0.558	0.151	0.177	0.131	0.044
	0.636	0.176		0.164	0.054
	0.711	0.192		0.205	0.066
	0.796			0.270	0.083
353.2	0.097	0.022	0.027	0.017	0.007
	0.173	0.040	0.049	0.032	0.012
	0.250	0.060	0.073	0.049	0.018
	0.324	0.080	0.095	0.067	0.024
	0.401	0.101	0.113	0.088	0.031
	0.479	0.123		0.113	0.039
	0.550	0.143		0.140	0.048
	0.626	0.161		0.175	0.059
	0.714			0.226	0.074
	0.796				0.090

Table 5. Solubility of Benzene in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc)

		w_1			
T/K	a_1	PI	PIB	PBMA	PVAc
293.3	0.359	0.072	0.063	0.117	
	0.394	0.081	0.071	0.132	
	0.488	0.108	0.092	0.174	
	0.534	0.133	0.110	0.207	
	0.636	0.167	0.135	0.249	
	0.719	0.211	0.170	0.325	
313.2	0.248	0.046	0.046	0.078	0.031
	0.325	0.068	0.064	0.108	0.054
	0.400	0.092	0.083	0.139	0.080
	0.477	0.120	0.105	0.175	0.106
	0.549	0.150	0.126	0.210	0.134
	0.627	0.185	0.142	0.269	0.171
	0.701			0.312	0.215
333.2	0.199	0.044	0.038	0.056	0.038
	0.292	0.071	0.058	0.087	0.060
	0.416	0.111	0.082	0.135	0.092
	0.489	0.138	0.092	0.171	0.115
	0.580	0.172		0.228	0.146
	0.680	0.208			
353.2	0.097	0.029	0.020	0.031	0.019
	0.172	0.053	0.031	0.059	0.037
	0.247	0.077		0.087	0.055
	0.328	0.104		0.119	0.078
	0.396	0.127		0.152	0.100
	0.482	0.155		0.200	0.127
	0.555	0.173		0.219	

Table 6. Solubility of Toluene in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc)

		w_1			
T/K	a_1	PI	PIB	PBMA	PVAc
293.2	0.516	0.134	0.107	0.174	
	0.562	0.157	0.124	0.204	
	0.608	0.175	0.141	0.230	
	0.658	0.190	0.158	0.252	
	0.689	0.200	0.171	0.268	
	0.752	0.218	0.199	0.304	
	0.799	0.231		0.347	
313.2	0.243	0.059	0.051	0.075	0.027
	0.325	0.082	0.071	0.107	0.052
	0.399	0.105	0.092	0.137	0.075
	0.469	0.126	0.115	0.169	0.096
	0.542	0.148	0.142	0.204	0.117
	0.615	0.170	0.172	0.240	0.141
	0.697			0.302	0.177
	0.776			0.365	0.221
333.2	0.095	0.016	0.014	0.019	0.009
	0.172	0.032	0.029	0.039	0.021
	0.246	0.051	0.047	0.062	0.035
	0.330	0.073	0.070	0.092	0.051
	0.401	0.095	0.091	0.119	0.067
	0.483	0.118	0.117		0.087
	0.547	0.135	0.137	0.182	0.104
	0.632			0.226	0.133
	0.713			0.276	0.161
	0.801			0.326	
353.2	0.098	0.025	0.026	0.030	0.016
	0.172	0.045	0.047	0.055	0.030
	0.248	0.065	0.069	0.083	0.045
	0.324	0.085	0.089	0.112	0.062
	0.409	0.107		0.148	0.084
	0.494	0.130		0.189	0.107
	0.555	0.145		0.224	0.125
	0.639	0.169		0.272	

For each solubility data point, the mass fraction was calculated by using eq 2. The solvent activity was obtained by equating the fugacities of the solvent in the vapor and solution phases. The polymers can be considered as nonvolatile, so by assuming the vapor phase to be pure solvent and estimating the pure solvent fugacity through use of second virial coefficient, the activity of the solvent was obtained

$$a_1 = \frac{P_1}{{P_1}^{S}} \exp\left[\frac{-\, B_1({P_1}^{S} - P_1)}{RT}\right] \tag{3}$$

where 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 the vapor pressure of the solvent at the temperature of the sorption cell and R is the gas constant. The vapor pressures were calculated from the Wagner equation with constants given by Reid et al.[15] B_1 is the second virial coefficient of the solvent and was obtained from the correlation of Tsonopoulos.[16]

Materials. All solvents were obtained from Katayama Chemical with gas chromatography grade purities of 98% for octane and cyclopentane, 99.5% for cyclohexane, benzene, and toluene, and 99% for ethylbenzene and *p*-xylene and were used without further purification. The polymers (*cis*-1,4-polyisoprene, polyisobutylene, poly(*n*-butyl methacrylate) and poly(vinyl acetate)) were amorphous polymers obtained from Aldrich Chemical Co., Inc., whose characteristics are shown in Table 1.

Uncertainty Estimation. Experimental uncertainty in this experiment may arise in the frequency measurements and temperature measurements for both the solvent tank and the sorption cell. Uncertainty in temperature mea-

Table 7. Solubility of Ethylbenzene in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc)

		w_1			
T/K	a_1	PI	PIB	PBMA	PVAc
293.2	0.556	0.145	0.125	0.200	
	0.589	0.161	0.139	0.219	
	0.668	0.196	0.171	0.256	
	0.735	0.229	0.204	0.311	
313.2	0.182	0.041	0.041	0.057	0.012
	0.250	0.059	0.058	0.081	0.022
	0.326	0.079	0.077	0.107	0.035
	0.402	0.102	0.097	0.135	0.049
	0.477	0.130	0.122	0.167	0.066
	0.542	0.155	0.143	0.193	0.079
	0.617	0.186	0.166		0.097
	0.689	0.215			0.116
	0.765				0.142
333.2	0.100	0.023	0.024	0.031	0.013
	0.178	0.044	0.046	0.056	0.026
	0.255	0.069	0.069	0.084	0.040
	0.333	0.098	0.095	0.115	0.054
	0.404	0.125	0.116	0.144	0.069
	0.485	0.155		0.176	0.086
	0.569	0.187		0.219	0.106
	0.638	0.209		0.265	0.127
	0.708			0.295	0.150
	0.798				0.184
353.2	0.099	0.030	0.029	0.032	0.016
	0.176	0.058	0.053	0.060	0.030
	0.257	0.088	0.075	0.090	0.045
	0.340	0.118	0.075	0.122	0.061
	0.411	0.142	0.086	0.152	0.078
	0.489	0.170		0.192	0.096
	0.565	0.191		0.233	0.118
	0.638			0.247	0.141

Table 8. Solubility of *p*-xylene in *cis*-1,4-Polyisoprene (PI), Polyisobutylene (PIB), Poly(*n*-butyl methacrylate) (PBMA), and Poly(vinyl acetate) (PVAc)

		w_1			
T/K	a_1	PI	PIB	PBMA	PVAc
293.2	0.502	0.146	0.117	0.170	
	0.526	0.158	0.127	0.183	
	0.550	0.168	0.137	0.197	
	0.599	0.185	0.155	0.221	
	0.634	0.198	0.171	0.240	
	0.656	0.206	0.182	0.251	
	0.692	0.218	0.201	0.269	
	0.724	0.228	0.219	0.288	
	0.743	0.234	0.228	0.301	
313.2	0.182	0.046	0.041	0.061	
	0.245	0.065	0.056	0.085	
	0.324	0.089	0.077	0.121	
	0.400	0.113	0.100	0.155	0.044
	0.466	0.134	0.124	0.184	0.062
	0.532	0.155	0.151	0.215	0.081
	0.613	0.181	0.186	0.245	0.104
	0.690	0.207		0.286	0.129
	0.759			0.314	0.157
333.2	0.097	0.025	0.023	0.028	0.011
	0.177	0.048	0.044	0.053	0.023
	0.255	0.070	0.066	0.079	0.035
	0.333	0.092	0.091	0.108	0.049
	0.415	0.114	0.120	0.141	0.065
	0.489	0.134	0.145	0.172	0.080
	0.578	0.161		0.213	0.102
	0.647	0.180		0.257	0.123
	0.725			0.319	0.154
	0.798				0.188
353.2	0.099	0.027	0.038	0.032	0.017
	0.172	0.049	0.065	0.057	0.029
	0.258	0.075	0.090	0.086	0.044
	0.331	0.098		0.113	0.058
	0.410	0.120		0.140	0.073
	0.492	0.142		0.171	0.089
	0.565	0.158		0.200	0.103

surement including its control was within ±0.05 K. Fluctuations in the frequency at equilibrium were ±(1 to 5) Hz throughout the experiment. Error analysis shows that the maximum uncertainty in the mass fraction of solvent was ±0.002. Considering the uncertainty in temperature measurements, vapor pressure correlation and Tsonopolous correlation for second virial coefficients, the uncertainty in solvent activity was found to be less than ±0.009.

Results and Discussion

Experimental solubility data for 28 solvent + polymer systems at temperatures of (293.2, 313.2, 333.2, and 353.2) K are presented through Tables 2−8. For systems containing poly(vinyl acetate), the data at 293.2 K were not measured because the equilibrium temperature is lower than the glass temperature.

The present results were compared with existing literature data for the systems of benzene + *cis*-1,4-polyisoprene,[17,18] benzene + polyisobutylene,[5,17−19] cyclohexane + polyisobutylene,[5,17−19] and benzene + poly(vinyl acetate).[20,21] For the last three systems our data agreed well with literature data with magnitude within ±3%. For the cyclohexane + polyisobutylene system, available the literature data at temperatures (273.2, 298.2, 313.2, and 373.2) K did not show significant temperature effects as presented in Figure 2. This is also presented by our data in the temperature range (293.2 to 353.2) K. Since the chemical structure of cyclohexane is close to that of repeating unit of polyisobutylene, it may be assumed that this system has zero enthalpy of mixing affecting in vanishing the temperature effects. Therefore, the comparison is reasonable. However, for benzene + *cis*-1,4-polyisoprene system, the solubilities observed by Eichinger and Flory[17] were somewhat greater and those observed by Bonner and Prausnitz[18] were somewhat lower than our data.

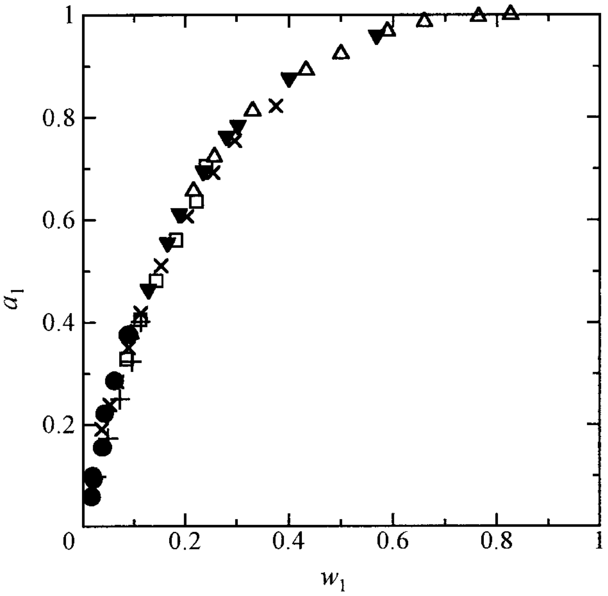

Figure 2. Activity of cyclohexane a_1 in cyclohexane (1) + polyisobutylene (2) at mass fraction w_1 and comparison with literature data. This work: □, T/K = 313.2; +, T/K = 353.2. Literature data: ▼, T/K = 298.2;[17] ×, T/K = 311.2;[5] △, T/K = 313.2;[19] ●, T/K = 373.2.[18]

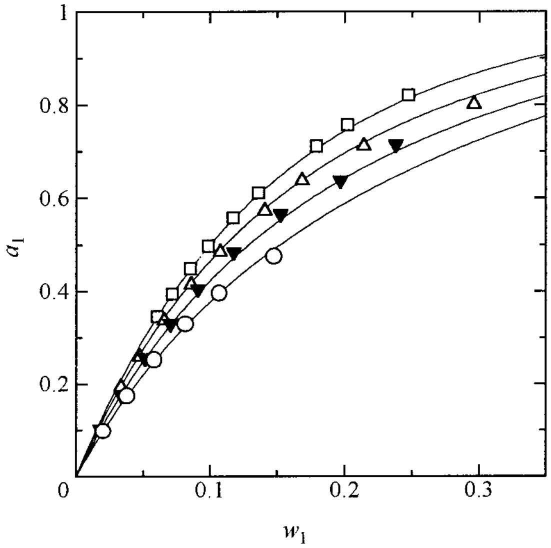

Figure 3. Activity of cyclopentane a_1 in cyclopentane (1) + poly(*n*-butyl methacrylate) (2) at various temperatures: □, T/K = 293.2; △, T/K = 313.2; ▼, T/K = 333.2 K; ○, T/K = 353.2 K; lines = calculated by the UNIQUAC equation.

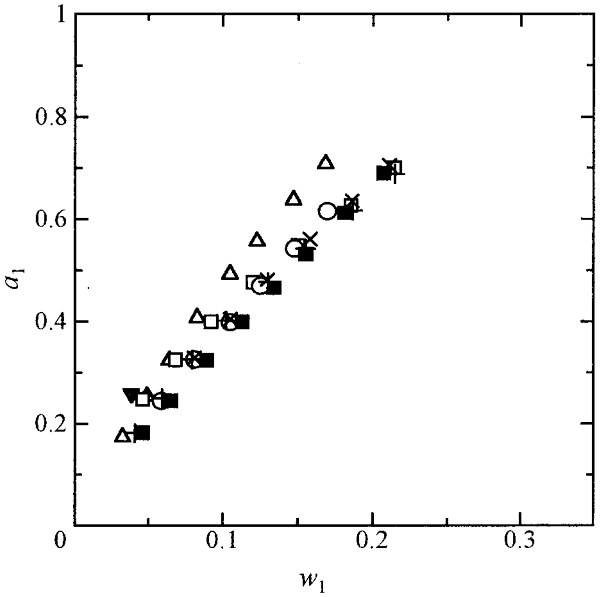

Figure 4. Activities of solvents a_1 at 313.2 K: △, octane (1) + *cis*-1,4-polyisoprene (2); ▼, cyclopentane(1) + *cis*-1,4-polyisoprene (2); ×, cyclohexane (1) + *cis*-1,4-polyisoprene (2); □, benzene (1) + *cis*-1,4-polyisoprene (2); ○, toluene (1) + *cis*-1,4-polyisoprene (2); +, ethyl benzene (1) + *cis*-1,4-polyisoprene (2), ■, *p*-xylene (1) + *cis*-1,4-polyisoprene (2).

For all systems studied, the solubility increases with increased temperature as shown in Figure 3 for the solubility of cyclopentane in poly(*n*-butyl methacrylate). For the nonpolar polymers studied, the solubilities of the solvents do not show significant difference as shown in Figures 4 and 5. For polar polymers studied, however, the solubilities of aromatic solvents are higher than those of alkane and cycloalkane solvents as shown in Figures 6 and 7, and the solubility of the solvents increases in order of octane < cycloalkane < aromatic compounds. All solvents studied show the lowest solubilities in poly(vinyl acetate) among the four polymers.

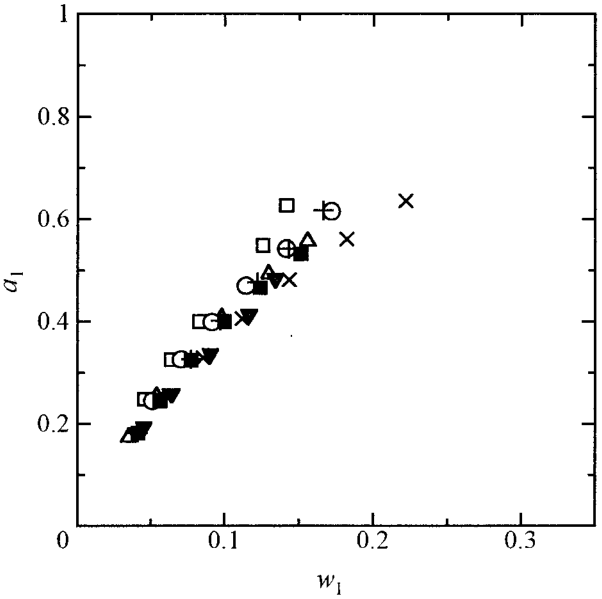

Figure 5. Activities of solvents a_1 at 313.2 K: △, octane (1) + polyisobutylene (2); ▼, cyclopentane (1) + polyisobutylene (2); ×, cyclohexane (1) + polyisobutylene (2); □, benzene (1) + polyisobutylene (2); ○, toluene (1) + polyisobutylene (2); +, ethyl benzene (1) + polyisobutylene (2); ■, *p*-xylene (1) + polyisobutylene (2).

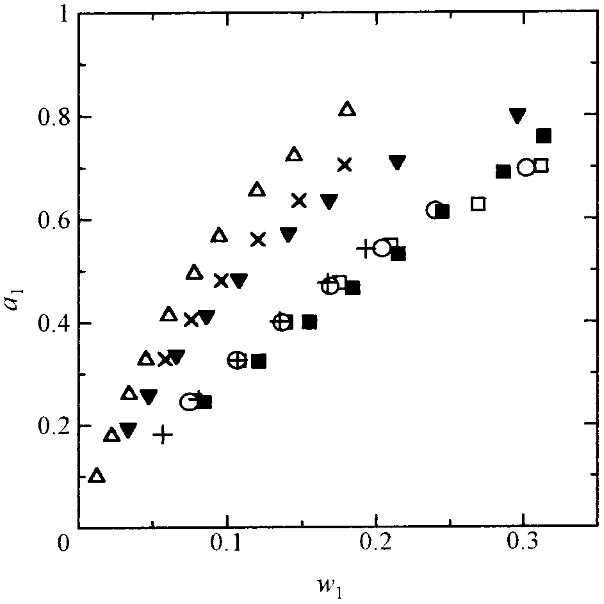

Figure 6. Activities of solvents a_1 at 313.2 K: △, octane (1) + poly(*n*-butyl methacrylate) (2); ▼, cyclopentane (1) + poly(*n*-butyl methacrylate) (2); ×, cyclohexane (1) + poly(*n*-butyl methacrylate) (2); □, benzene (1) + poly(*n*-butyl methacrylate) (2); ○, toluene (1) + poly(*n*-butyl methacrylate) (2); +, ethyl benzene (1) + poly(*n*-butyl methacrylate) (2); ■, *p*-xylene (1) + poly(*n*-butyl methacrylate) (2).

The UNIQUAC equation[22] was chosen to correlate our data because the combinatorial contribution of the equation is applicable to account for the large difference in molecular size between solvent and polymer. Recently, the equation has been used for correlating of vapor–liquid equilibria for solvent–polymer systems elsewhere, for example, in the Polymer Data Collection of Wen et al.[1] and by Kim et al.[23] for correlating their experimental data. The UNIQUAC interaction parameters, a_{ij}, defined by a linear function of temperature, were used

$$a_{ij} = a_{ij}^{(0)} + a_{ij}^{(1)}(T/\mathrm{K} - 273.15) \tag{4}$$

where $a_{12}^{(0)}$, $a_{12}^{(1)}$, $a_{21}^{(0)}$, and $a_{21}^{(1)}$ are temperature-independent constants. The best fit UNIQUAC parameters,

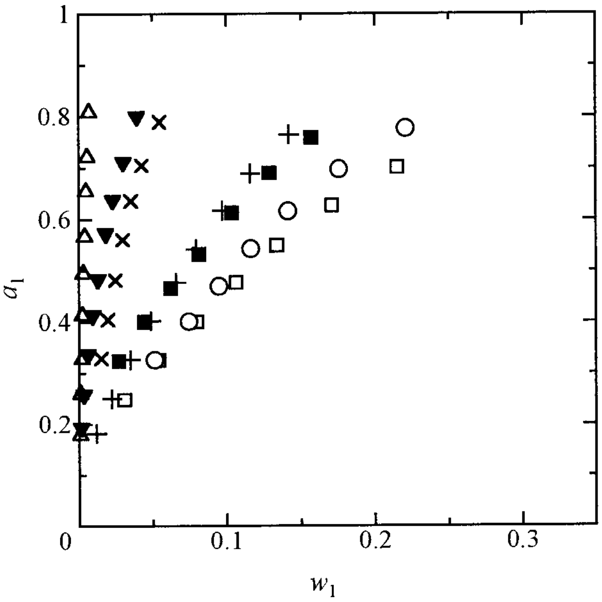

Figure 7. Activities of solvents a_1 at 313.2 K: △, octane (1) + poly(vinyl acetate) (2); ▼, cyclopentane (1) + poly(vinyl acetate) (2); ×, cyclohexane (1) + poly(vinyl acetate) (2); □, benzene (1) + poly(vinyl acetate) (2); ○, toluene (1) + poly(vinyl acetate) (2); +, ethyl benzene (1) + poly(vinyl acetate) (2); ■, *p*-xylene (1) + poly(vinyl acetate) (2).

Table 9. Temperature-Independent Parameters of the UNIQUAC Equation in Eq 4, and Average Absolute Deviation (AAD) between Measured and Calculated Solvent Activities

polymer	solvent	$a_{12}^{(0)}$/K	$a_{12}^{(1)}$	$a_{21}^{(0)}$/K	$a_{21}^{(1)}$	AAD^c/%
PI^a	octane	214.21	1.21	−113.19	−0.54	2.9
	cyclopentane	7608.58	41.78	−281.72	1.69	7.0
	cyclohexane	247.35	3.00	−132.87	−1.02	1.3
	benzene	−157.54	2.50	319.64	−3.82	3.1
	toluene	56.81	4.17	−16.06	−2.02	6.1
	ethylbenzene	201.10	−2.84	−105.80	1.96	2.7
	p-xylene	425.99	13.97	−218.79	−1.28	1.9
PIB^a	octane	1.35	2.25	30.46	−1.75	3.6
	cyclopentane	−56.23	0.44	133.36	−0.72	3.3
	cyclohexane	−19.77	0.61	74.99	−0.80	1.7
	benzene	−0.13	0.82	113.35	−0.57	4.3
	toluene	−137.24	1.72	272.92	−2.62	7.1
	ethylbenzene	107.76	1.72	−21.25	−1.51	2.7
	p-xylene	−120.07	1.89	218.24	−2.84	3.2
PBMA^a	octane	−26.24	−0.43	92.90	0.37	1.9
	cyclopentane	3.46	−2.13	75.64	2.49	1.0
	cyclohexane	−19.09	−0.72	103.40	0.59	0.9
	benzene	−164.65	1.77	249.87	−2.67	2.7
	toluene	−16.68	2.09	39.17	−1.75	6.8
	ethylbenzene	176.43	2.65	−118.21	−1.45	1.2
	p-xylene	361.54	0.90	−197.84	−0.60	3.8
PVAc^b	octane	−271.58	0.18	768.63	−2.69	14.0
	cyclopentane	−235.32	0.78	768.78	−4.28	11.0
	cyclohexane	−80.53	−0.17	302.78	−0.48	3.7
	benzene	−222.59	1.11	490.28	−3.26	3.2
	toluene	−330.12	3.14	647.23	−6.07	4.7
	ethylbenzene	−142.54	0.57	327.30	−1.91	5.7
	p-xylene	−205.12	1.89	395.21	−3.43	3.6
	Overall					4.1

[a] Temperature range: 293.2−353.2 K. [b] Temperature range: 313.2−353.2 K. [c] AAD = $(1/N)|a_1^{calcd} - a_1^{expt}|/a_1^{expt} \times 100$; N = number of data points; superscripts calcd and expt denote the calculated and experimental values.

temperature range, and average absolute deviations (AAD) between measured and calculated activities are summarized in Table 9. Overall AAD was 4.1% for all the systems. The highest AAD was shown in octane + poly(vinyl acetate) system with 14.0%, because of the low solubility. The temperature-independent parameters obtained in this work will be more convenient in engineering applications, since solvent activity can be accurately calculated at various temperatures by using one set of parameters.

Conclusion

Solubility data of seven organic solvents (octane, cyclopentane, cyclohexane, benzene, toluene, ethylbenzene, and *p*-xylene) in four polymers (*cis*-1,4-polyisoprene, polyisobutylene, poly(*n*-butyl methacrylate), and poly(vinyl acetate)) have been measured at (293.2, 313.2, 333.2, and 353.2) K with a piezoelectric quartz crystal microbalance apparatus. The experimental solubility data for benzene and cyclohexane in PIB agreed well with the literature data. The solubility of each solvent studied appeared to be the lowest in PVAc. Correlation results were represented using UNIQUAC equation with overall AAD of 4.1% for activities.

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