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Sorption of Benzene, Dichloromethane, *n*-Propyl Acetate, and 2-Butanone by Poly(methyl methacrylate), Poly(ethyl methacrylate), and Their Copolymers at 323.15 K Using a Quartz Crystal Balance

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ABSTRACT: Isothermal solubilities of benzene, dichloromethane, *n*-propyl acetate, and 2-butanone in poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and two different PMMA/PEMA copolymers at 323.15 K are reported. Data were measured in the concentrated-polymer regime using a quartz crystal balance and are represented by a modified Flory−Huggins equation to within experimental error. The model parameters show a trend with copolymer composition.

INTRODUCTION

As the first part of a study of how the activities of solvents in solution with copolymers vary with copolymer group composition, we report sorption data at 323.15 K for benzene, dichloromethane, *n*-propyl acetate, and 2-butanone in poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and two PMMA/PEMA copolymers of different composition. The data were obtained in the concentrated-polymer regime using the same quartz crystal balance (QCB) used to obtain the activities of benzene, toluene, and chloroform in polystyrene[1] and of benzene, tetrahydrofuran, and 2-butanone in poly(vinyl acetate).[2]

The activities of 2-butanone in PMMA at 313.15 K have been reported by Tait and Abushihada[3] for 2-butanone mass fractions between approximately 0.03 and 0.2. Sé and Aznar[4] measured vapor−liquid equilibria for benzene in PMMA and in PEMA at (303.15 and 313.15) K for solvent mass fractions between approximately 0.01 and 0.1. Infinite-dilution activity coefficients have been reported by Tochigi et al.[5] for benzene and 2-butanone in PMMA at temperatures from (453 to 493) K, by Hao et al.[6] for benzene in PMMA from (363 to 383) K, and by Hao et al.[6] for benzene and 2-butanone in PEMA at 417.7 K. We were unable to locate any activity data for any of these solvents in PMMA/PEMA copolymers.

EXPERIMENTAL SECTION

Materials. All polymers and copolymers were obtained from Polysciences, Inc. The weight-average molecular weights of PMMA and PEMA were 185 000 and 340 000, respectively. PMMA/PEMA (60:40) is a copolymer of PMMA and PEMA with $100\,w_{\mathrm{PMMA}} = 60$, while PMMA/PEMA (30:70) is a copolymer with $100\,w_{\mathrm{PMMA}} = 30$. Both copolymers had weight-average molecular weights of 250 000. Benzene, dichloromethane, *n*-propyl acetate, and 2-butanone were HPLC-grade with mass-fraction purity of 0.9995. They were obtained from Aldrich Chemical Co. and degassed as described by Bhethanabotla and Campbell.[7] No further purification was attempted. The quartz crystals used had a base frequency of 5 MHz and were supplied by Crystek Corporation (Fort Myers, FL).

Apparatus and Procedure. The experimental apparatus and procedure have been described fully in an earlier publication.[1] The basic measurement principle is that mass deposited on the surface of a piezoelectric quartz crystal induces a frequency shift in the crystal. Briefly, the polymer to be studied was dissolved in chloroform and then coated onto the quartz crystal. After the chloroform was completely evaporated, the frequency shift Δf_0 due to the presence of the polymer coating was determined under vacuum. The crystal was then exposed to the vapor of the desired solvent at a known temperature and pressure, and the additional frequency shift Δf due to sorption of the solvent by the polymer was determined at equilibrium. The mass fraction of the solvent in the polymer, w_1, was then calculated from[1]

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

For the measurements reported here, the Δf_0 values ranged from (1486 to 2389) Hz and were mostly within the range from (1800 to 2200) Hz.

Solvent vapor was generated by placing the solvent in a cell maintained at a temperature below 323.15 K. The sorption cell containing the polymer-coated crystal was connected via a heated line to the solvent cell but maintained at 323.15 K. Thus, the pressure in the system was equal to the vapor pressure of the solvent at the temperature of the solvent cell. The pressure was varied at constant sorption cell temperature either by increasing the temperature of the solvent cell (a sorption run) or decreasing it (a desorption run). At each point, the activity of the solvent in the polymer, a_1, was calculated from

$$a_1 = \frac{P}{P_1^{\mathrm{sat}}} \exp\left[-\frac{B_{11}}{RT}(P_1^{\mathrm{sat}} - P)\right] \tag{2}$$

where B_{11} is the second virial coefficient of the solvent at the sorption cell temperature and P and P_1^{sat} are solvent pressures

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Table 1. Coefficients in the Vapor Pressure Equation (Equation 3) and Solvent Second Virial Coefficients B_{11} Used in the Activity Calculations

solvent	A	B	C	D	$B_{11}/\text{cm}^3\cdot\text{mol}^{-1}$
benzene	−6.98273	1.33213	−2.62863	−3.33399	−1292
dichloromethane	−7.36864	1.76727	−3.34295	−1.43530	−678
n-propyl acetate	−7.85524	1.43936	−4.30187	−3.04832	−2127
2-butanone	−7.71476	1.71061	−3.68770	−0.75169	−1908

evaluated from a literature vapor pressure correlation for the solvent at the solvent cell and sorption cell temperatures, respectively. Here, the correlation of Tsonopoulos[8] was used to estimate B_{11}, and P and P_1^{sat} were calculated using the Wagner equation:

$$\ln\left(\frac{P}{P_C}\right) = (1-x)^{-1}[Ax + Bx^{1.5} + Cx^3 + Dx^6] \qquad (3)$$

where $x = 1 - T/T_C$ and T_C and P_C are the critical temperature and pressure of the solvent, respectively. Values of the second virial coefficients and the parameters in eq 3, which were taken from Reid et al.,[9] are given in Table 1 for the four solvents studied here.

Equilibration times for the sorption of benzene, 2-butanone, and *n*-propyl acetate in PMMA were (1.5 to 2) days at lower solvent activities and (2 to 4) h at the highest. Because of its higher solvating power and vapor pressure, the sorption equilibration times for dichloromethane were shorter [(2 to 4) h at lower activities and (2 to 5) min at higher ones]. The desorption equilibration times were comparable to those for sorption at higher solvent activities but shorter at lower activities. However, this was accompanied by hysteresis between sorption and desorption at low solvent activities, as discussed later.

For all of the solvents in PEMA, the equilibration times for sorption and desorption were comparable and were 12 h or less. Equilibration times for the solvents in the copolymers fell between the corresponding times for the pure polymers.

The solvent and sorption cell temperatures were maintained to ± (0.01 and 0.3) K, respectively. To estimate the uncertainty in solvent activity, the effects of gas nonideality were neglected and the uncertainty in solvent cell temperature was neglected relative to the uncertainty in the sorption cell temperature; this allows the uncertainty in the solvent activity, σ_{a1}, to be expressed as

$$\left|\frac{\sigma_{a_1}}{a_1}\right| = \left(\frac{\mathrm{d}\ln P_1^{\text{sat}}}{\mathrm{d}T}\right)_{323.15\text{K}} \sigma_T \qquad (4)$$

where σ_T = 0.3 K is the uncertainty in the sorption cell temperature. The values of the vapor pressure derivatives were similar for the four solvents, resulting in an uncertainty of approximately ± 2 % in the solvent activity. To within first order, the following expression for the uncertainty in the solvent mass fraction, σ_{w_1}, can be derived from eq 1:

$$\sigma_{w_1} = \frac{\left(\dfrac{\sigma_{\Delta f}}{\Delta f_0} + \dfrac{w_1}{1-w_1}\dfrac{\sigma_{\Delta f_0}}{\Delta f_0}\right)}{\left(1 + \dfrac{w_1}{1-w_1}\right)^2} \qquad (5)$$

where $\sigma_{\Delta f}$ and $\sigma_{\Delta f_0}$ are uncertainties in Δf and Δf_0, respectively. The uncertainties in Δf varied from ± 1 Hz at the lowest w_1 to ± 5 Hz at the highest. The maximum uncertainties in Δf_0 were from (15 to 30) Hz. These uncertainties translate to a maximum uncertainty of 0.009 in the solvent mass fraction.

Table 2. Experimental Mass Fractions (w_1) of Benzene (1) in PMMA, PEMA, or One of Two PMMA/PEMA Copolymers (2) as Functions of the Benzene Activity (a_1) at 323.15 K; Also Included Are the Numbers of Sorption and Desorption Runs ($n_{\text{sorp}}/n_{\text{desorp}}$) and the Average Standard Deviation in Measurements of w_1

	w_1			
a_1	PMMA	PMMA/PEMA (60:40)	PMMA/PEMA (30:70)	PEMA
0.191				0.061
0.233				0.072
0.283			0.088	0.088
0.340		0.087	0.106	0.107
0.408		0.106	0.129	0.131
0.485		0.133	0.158	0.162
0.528		0.151	0.177	0.181
0.575	0.139	0.172	0.198	0.205
0.624	0.156	0.197	0.226	0.233
0.675	0.175	0.226	0.260	0.266
0.731	0.198	0.263	0.297	0.305
0.792	0.226			
$n_{\text{sorp}}/n_{\text{desorp}}$	2/2	2/2	3/3	3/3
av w_1 std dev	0.002	0.003	0.003	0.005

The 5 MHz crystals utilized in this study were not as sensitive as the 10 MHz ones used in the earlier study,[1] but they provided better frequency stability. Viscoelastic effects were also expected to be smaller for these lower-frequency crystals. The Saurbrey model utilized in this study to interpret the QCB response assumes that the mass inertially coupled to the device surface is the sole contributor to the device response. When the adsorbed polymer is softened by absorption of solvent, there is the possibility of viscoelastic contributions to the frequency shifts. We utilized the two terminal Butterworth−van Dyke equivalent electrical circuit model for the polymer/solvent-loaded QCB to understand these viscoelastic contributions. In studies with several polymer/solvent systems,[10] we have empirically established that the motional resistance change upon solvent absorption into the polymer must stay small for the mass loading to be in the inertial regime. Specifically, infinite-dilution activity coefficient data gathered using this technique compared well with those obtained utilizing other techniques, provided the motional resistance upon sorption stayed less than about 200 Ω. This was typical for the polymers and range of solvent concentrations reported in this contribution. Hence, viscoelastic effects were expected to be negligible for these reported data. The utilization of the lower-frequency crystals in this study also was expected to contribute positively to this situation, extending the range of solvent concentrations for which reliable sorption data can be gathered.

RESULTS

Solvent mass fractions in each of the two polymers and two copolymers are given as functions of the solvent activity for benzene, dichloromethane, *n*-propyl acetate, and 2-butanone in Tables 2, 3, 4, and 5, respectively. Also shown in these tables are the numbers of sorption runs and desorption runs

Table 3. Experimental Mass Fractions (w_1) of Dichloromethane (1) in PMMA, PEMA, or One of Two PMMA/PEMA Copolymers (2) as Functions of the Dichloromethane Activity (a_1) at 323.15 K; Also Included Are the Numbers of Sorption and Desorption Runs ($n_{\mathrm{sorp}}/n_{\mathrm{desorp}}$) and the Average Standard Deviation in Measurements of w_1

	w_1			
a_1	PMMA	PMMA/PEMA (60:40)	PMMA/PEMA (30:70)	PEMA
0.142		0.076	0.079	0.083
0.179		0.092	0.099	0.105
0.224	0.089	0.112	0.125	0.132
0.278	0.105	0.137	0.157	0.164
0.342	0.126	0.172	0.194	0.203
0.415	0.157	0.215	0.242	0.250
0.501	0.195	0.267	0.299	0.308
0.539			0.326	0.337
0.602	0.245	0.334	0.371	0.380
0.669	0.279	0.385	0.422	0.428
0.715	0.304	0.427	0.462	0.464
0.766	0.330	0.476	0.503	0.507
0.819	0.354			
$n_{\mathrm{sorp}}/n_{\mathrm{desorp}}$	3/3	2/2	2/2	2/1
av w_1 std dev	0.006	0.002	0.002	0.002

Table 4. Experimental Mass Fractions (w_1) of n-Propyl Acetate (1) in PMMA, PEMA, or One of Two PMMA/PEMA Copolymers (2) as Functions of the 2-Butanone Activity (a_1) at 323.15 K; Also Included Are the Numbers of Sorption and Desorption Runs ($n_{\mathrm{sorp}}/n_{\mathrm{desorp}}$) and the Average Standard Deviation in Measurements of w_1

	w_1			
a_1	PMMA	PMMA/PEMA (60:40)	PMMA/PEMA (30:70)	PEMA
0.284		0.071	0.077	0.077
0.351		0.084	0.094	0.095
0.429		0.103	0.116	0.118
0.474		0.115	0.130	0.133
0.524		0.132	0.146	0.151
0.577		0.151	0.166	0.172
0.632	0.123	0.172	0.191	0.199
0.694	0.139	0.199	0.221	0.230
$n_{\mathrm{sorp}}/n_{\mathrm{desorp}}$	2/0	2/2	4/4	2/2
av w_1 std dev	0.0003	0.002	0.003	0.003

for each solvent + polymer system. All of the mass fractions given in these tables were averaged over all of the sorption and desorption data at equal solvent activities. Standard deviations in the w_1 values at a given activity were computed and then averaged over all points to obtain the average standard deviations shown in Tables 2 through 5. All of these standard deviations are within the experimental uncertainty in w_1.

Table 5. Experimental Mass Fractions (w_1) of 2-Butanone (1) in PMMA, PEMA, or One of Two PMMA/PEMA Copolymers (2) as Functions of the n-Propyl Acetate Activity (a_1) at 323.15 K; Also Included Are the Numbers of Sorption and Desorption Runs ($n_{\mathrm{sorp}}/n_{\mathrm{desorp}}$) and the Average Standard Deviation in Measurements of w_1

	w_1			
a_1	PMMA	PMMA/PEMA (60:40)	PMMA/PEMA (30:70)	PEMA
0.184			0.054	0.055
0.225			0.062	0.064
0.275		0.063	0.072	0.075
0.332		0.074	0.086	0.089
0.400		0.089	0.102	0.108
0.476	0.102	0.110	0.125	0.132
0.520	0.112	0.124	0.139	0.146
0.567	0.125	0.139	0.156	0.163
0.617	0.142	0.159	0.177	0.184
0.669	0.165	0.182	0.200	0.211
0.726	0.193	0.212	0.232	0.245
$n_{\mathrm{sorp}}/n_{\mathrm{desorp}}$	2/2	2/2	3/3	2/2
av w_1 std dev	0.002	0.002	0.004	0.002

Sorption/desorption hysteresis in concentrated polymer solutions has been noted by Bonner and Prausnitz,[11] Jessup,[12] and others and has been attributed to the glassy nature of some polymers. Below the glass transition temperature, hysteresis between sorption and desorption exists and is attributed to irreversible plastic deformation. The glass transition temperatures of PMMA and PEMA are (378 and 336) K, respectively, which are above the sorption temperature used here. However, the glass transition temperature is lowered because of the presence of solvent molecules. It would therefore be expected that there should be a particular solvent mass fraction for each isotherm for which the glass transition temperature has been lowered to the sorption temperature, with the result that hysteresis should exist for lower solvent mass fractions and be absent at higher mass fractions.

A series of t tests were performed on the data measured here to determine whether the sorption and desorption data belonged to different distributions, indicating hysteresis in the data. No hysteresis was evident for any of the solvents in PEMA or either of the copolymers. This is likely because the glass transition temperature of PEMA is only 13 K above the sorption temperature.

For benzene, dichloromethane, and 2-butanone in PMMA, hysteresis was observed at the lowest solvent mass fractions. In fact, the results for all three solvents in PMMA showed that hysteresis occurred below solvent mass fractions of approximately 0.1. Points where hysteresis occurred are not included in Tables 2 through 5. For n-propyl acetate in PMMA, only two sorption runs were made. Though they were in excellent agreement for all concentrations, we assume they exhibit the same sorption/desorption hysteresis behavior observed for the other solvents in PMMA. Thus, we have reported only the two data points for which w_1 exceeds 0.1 for this system.

■ DATA CORRELATION

For the purpose of providing a compact representation of the data reported here, the experimental solvent activities were fitted

Table 6. Molecular Weights (M) and Molar Volumes (V) of Solvents and Polymers

species	M/g·mol^{-1}	V/cm^3·mol^{-1}
	Solvents	
benzene	78.11	92.41
dichloromethane	84.93	64.44
n-propyl acetate	102.13	118.88
2-butanone	72.11	93.23
	Polymers	
PMMA	185000	156800
PMMA/PEMA (60:40)	250000	216200
PMMA/PEMA (30:70)	250000	221000
PEMA	340000	305900

Table 7. Parameters Used in the Modified Flory−Huggins Model (Equation 8) and Average Deviations between the Experimental Values of w_1 and Those Calculated Using Equation 8

system	A	B	avg dev
benzene (1) + PMMA (2)	0.791	0.305	0.0002
benzene (1) + PMMA/PEMA (60:40) (2)	0.335	0.240	0.002
benzene (1) + PMMA/PEMA (30:70) (2)	0.243	0.025	0.003
benzene (1) + PEMA (2)	0.226	0.008	0.002
dichloromethane (1) + PMMA (2)	0.715	0.081	0.003
dichloromethane (1) + PMMA/PEMA (60:40) (2)	0.007	−0.128	0.003
dichloromethane (1) + PMMA/PEMA (30:70) (2)	−0.141	−0.246	0.001
dichloromethane (1) + PEMA	−0.135	−0.313	0.002
n-propyl acetate(1) + PMMA/PEMA (60:40) (2)	0.771	0.230	0.002
n-propyl acetate(1) + PMMA/PEMA (30:70) (2)	0.639	0.145	0.002
n-propyl acetate(1) + PEMA (2)	0.536	0.182	0.002
2-butanone (1) + PMMA (2)	0.598	0.414	0.002
2-butanone (1) + PMMA/PEMA (60:40) (2)	0.596	0.254	0.003
2-butanone (1) + PMMA/PEMA (30:70) (2)	0.658	0.003	0.004
2-butanone (1) + PEMA (2)	0.575	−0.007	0.004

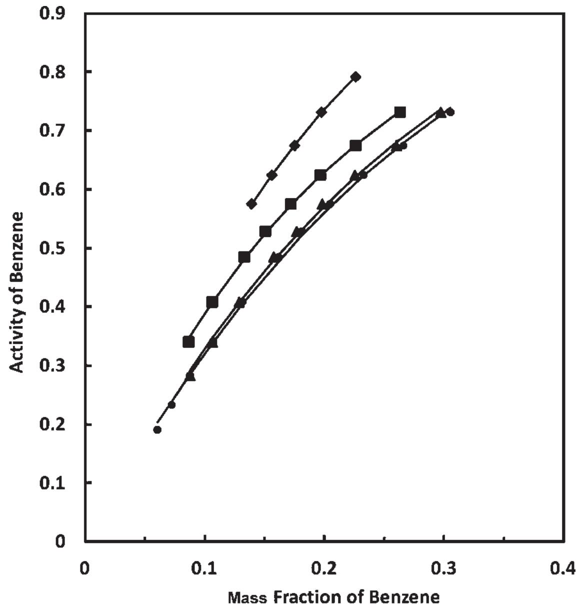

Figure 1. Experimental activities a_1 in benzene (1) + polymer (2) mixtures as functions of benzene mass fraction w_1 at 323.15 K: ◆, PMMA; ■, PMMA/PEMA (60:40); ▲, PMMA/PEMA (30:70); ●, PEMA. Solid curves are fits to eq 8.

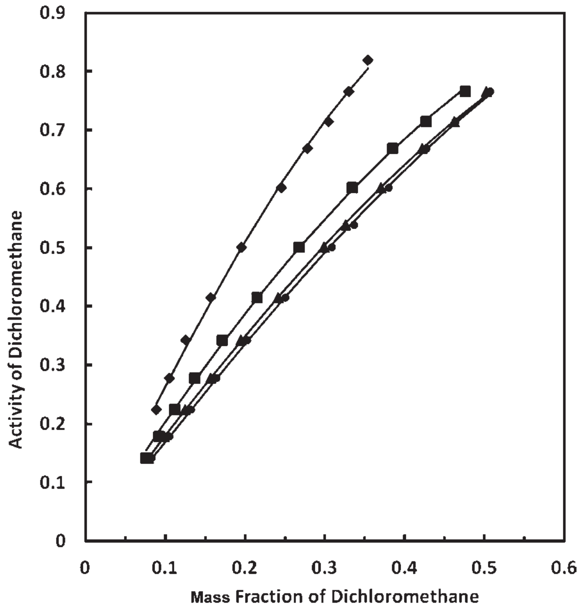

Figure 2. Experimental activities a_1 in dichloromethane (1) + polymer (2) mixtures as functions of dichloromethane mass fraction w_1 at 323.15 K: ◆, PMMA; ■, PMMA/PEMA (60:40); ▲, PMMA/PEMA (30:70); ●, PEMA. Solid curves are fits to eq 8.

to a modification of the Flory−Huggins activity model, in which the excess Gibbs energy, G^E, is given by

$$\frac{NG^E}{RT} = N_1 \ln\frac{\Phi_1}{X_1} + N_2 \ln\frac{\Phi_2}{X_2} + \Phi_1\Phi_2(N_1 + rN_2)[A\Phi_1 + B\Phi_2] \tag{6}$$

where N_i is the molar amount, X_i is the mole fraction, and Φ_i is the volume fraction of the solvent ($i = 1$) or polymer ($i = 2$). The variable $r = V_2/V_1$ is the ratio of molar volumes, and A and B are constants obtained by fitting the experimental data. The volume fraction of component i is expressed as

$$\Phi_i = \frac{V_iX_i}{\sum_j V_jX_j} \tag{7}$$

The molar volumes of the polymers were calculated as follows. Specific volumes were evaluated at 323.15 K using reported values of the density and thermal expansion coefficient for PMMA[13] and PEMA.[14] Specific volumes of the copolymers were then assumed to be a mass-fraction average of those of pure PMMA and PEMA. Molar volumes for all polymers were then calculated from the specific volume and the given molecular weights. Specific volumes of solvents were obtained using the modified Rackett equation.[15] For convenience, the molecular weights and molar volumes of all species are given in Table 6.

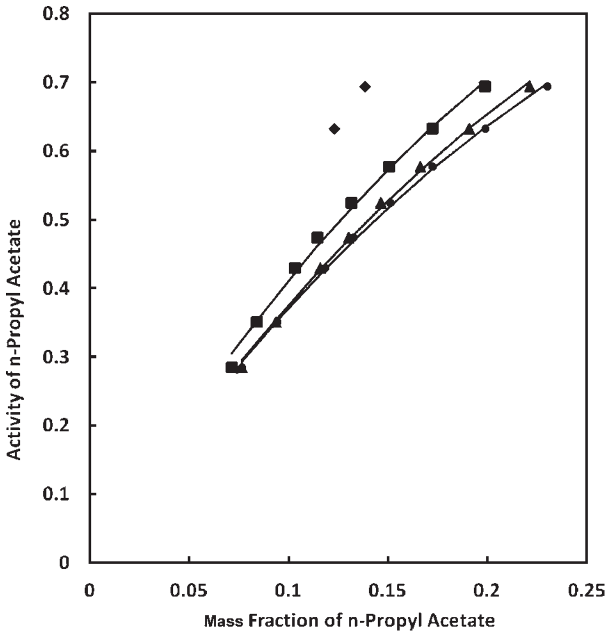

Figure 3. Experimental activities a_1 in *n*-propyl acetate (1) + polymer (2) mixtures as functions of *n*-propyl acetate mass fraction w_1 at 323.15 K: ◆, PMMA; ■, PMMA/PEMA (60:40); ▲, PMMA/PEMA (30:70); ●, PEMA. Solid curves are fits to eq 8.

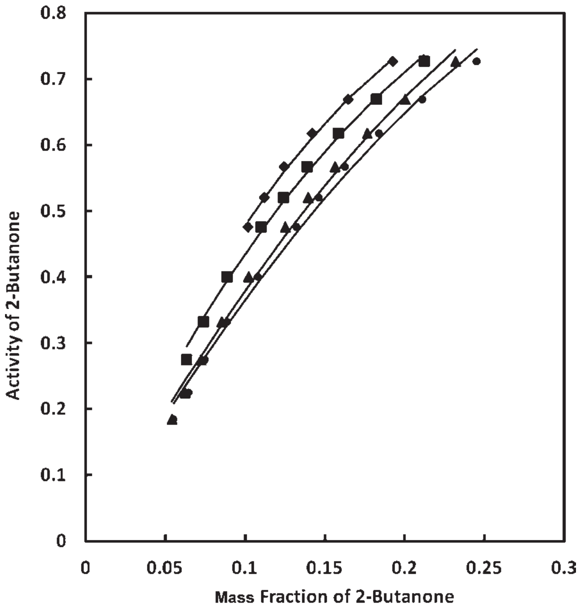

Figure 4. Experimental activities a_1 for 2-butanone (1) + polymer (2) mixtures as functions of 2-butanone mass fraction w_1 at 323.15 K: ◆, PMMA; ■, PMMA/PEMA (60:40); ▲, PMMA/PEMA (30:70); ●, PEMA. Solid curves are fits to eq 8.

The expression for solvent activity a_1 derived from eqs 6 and 7 is

$$\ln a_1 = \ln \Phi_1 + \left(1 - \frac{1}{r}\right)\Phi_2 + \left[2(A - B)\Phi_1 + B\right]\Phi_2^2 \tag{8}$$

The parameters A and B were determined by minimizing the sum of the squares of the differences between the experimental and calculated activities. It was necessary to convert the experimental mass fractions to volume fractions in these computations, and this was accomplished using the following expression:

$$\Phi_1 = \frac{w_1 \dfrac{M_2}{V_2}}{\dfrac{M_1}{V_1} - w_1\left(\dfrac{M_1}{V_1} - \dfrac{M_2}{V_2}\right)} \tag{9}$$

The values of A and B for each solvent + polymer pair are shown in Table 7, along with resulting average deviations between the experimental and calculated values of w_1. Comparisons of the experimental activities with those computed using eq 8 are shown in Figures 1 through 4. The values of A and B are not provided for *n*-propyl acetate + PMMA because there were only two data points for this system. For the other systems, the representation of the mass fraction is to within the experimental uncertainty in all cases. It can be seen from Table 7 that there are trends in the values of A and B with copolymer composition, with the values becoming larger as the fraction of PMMA increases.

■ CONCLUSION

The solvent mass fraction as a function of solvent activity at 323.15 K has been reported for benzene, dichloromethane, *n*-propyl acetate, and 2-butanone in PMMA, PEMA and two different PMMA/PEMA copolymers. The data are represented by a modified Flory−Huggins model to within experimental uncertainties. For a given solvent, the model parameters trend with composition of the copolymer, with higher positive values for PMMA that become progressively smaller, and sometimes negative, as the composition becomes higher in PEMA.

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