Determination of Solvent Activity in Poly(propylene glycol) + Methanol, + Ethanol, + 2-Propanol, and + 1-Butanol Solutions at 25 °C

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The activities of methanol, ethanol, 2-propanol, and 1-butanol in poly(propylene glycol) (PPG) (M_p: 1000) solutions have been measured by the isopiestic method at 25 °C. Sodium iodide and calcium chloride were used as the isopiestic standards for the calculation of activities. The original equation of Flory−Huggins and the modified Flory−Huggins equation with concentration dependent interaction parameters have been used for the correlation of obtained experimental solvent activity data. Better agreement with the experimental data was obtained using the modified Flory−Huggins equation.

Introduction

Phase equilibria play an important role in the processing and application of polymers. In this respect, a quantitative description of the vapor−liquid equilibrium (VLE) behavior in solvent + polymer systems is often necessary in order to design a polymer manufacturing process or to predict process performance.

VLE data for some polymer solutions have been compiled in ref 1, which contains VLE data for some PPG + solvent systems. Here, in regard to PPG + alcohol solutions, there are only a few vapor pressure data for PPG + methanol solutions for different molar masses of the polymer (from Lakhanpal et al.[2]). For instance, at 25 °C for PPG1120, the reported[2] vapor pressure data are limited to only four mass fractions of the polymer ranging from 0.1251 to 0.5434. There are no activity or vapor pressure data for PPG + ethanol solutions at 25 °C. Recently, a few vapor pressure data points of PPG + methanol and PPG + ethanol with polymer of molar mass 400 have been measured[3] at 30 °C with an apparatus based on the principle of electromicrobalance. In their vapor sorption measurements,[3] however, they only considered the methanol and ethanol mass fractions in the limited ranges 0.0354−0.1693 and 0.0282−0.1320, respectively. However, for solutions of PPG in 2-propanol and 1-butanol, there are no activity data in the literature. In the present report, activities of methanol, ethanol, 2-propanol, and 1-butanol in solutions of PPG having molar mass $M_p = 1000$ are measured by the improved isopiestic method at 25 °C. The results were correlated with a cubic equation, the Flory−Huggins (FH) equation,[4] and the modified FH equation,[5] with concentration dependent interaction parameters.

Experimental Procedure

All the chemicals were obtained from Merck, except PPG1000, which was obtained from Aldrich. Sodium iodide (GR, minimum 99.5% by mass) and calcium chloride (GR, minimum 99.5% by mass) were dried in an electrical oven at about 110 °C for 24 h prior to use. Methanol (GR, minimum 99.8% by mass), ethanol (GR, minimum 99.8% by mass), and 2-propanol (GR, minimum 99.7% by mass) were dehydrated according to Vogel.[6] 1-Butanol (GR, minimum 99.5% by mass) and PPG1000 were used without further purification. The density and refractive index of the alcohols were measured respectively with a vibrating-tube densimeter (Kyoto Electronic DA-210, Japan) and a refractometer (QUARTZ RS-232, Belgium). The results of these measurements, which are collected in Table 1, are in good agreement with the literature values. The number average relative molar mass of PPG was obtained, $M_p = 976$, with an NMR spectroscopic method. Geckeler and Arsalani[7] have recently used this technique for determination of the number of monomers in some hydrophilic polymers, from which the molar masses of the polymers can be calculated.

The isopiestic apparatus employed is essentially similar to the one used previously.[8] Recently, this technique has been used for the measurement of the activity of 2-propanol in 2-propanol + poly(ethylene glycol) systems with different molar masses of the polymer.[9] This apparatus consisted of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard NaI or $CaCl_2$ solutions, two flasks contained PPG solutions, and the central flask was used as an alcohol reservoir. The apparatus was held in a constant-temperature bath for at least 120 h for equilibration at (25.0 ± 0.005) °C. The temperature was controlled to within ±0.005 °C with a Heto temperature controller (Hetotherm PF, Heto Lab Equipment, Denmark). After equilibrium had been reached, the manifold assembly was removed from the bath and each flask was weighed with a high precision (10^{-7} kg) analytical balance (Shimatzu, 321-34553, Shimatzu Co., Japan). It was assumed that the equilibrium condition was reached when the differences between the mass fractions of each duplicate were less than 1%. In all cases, averages of the duplicate are reported as the total isopiestic mass fraction. The uncertainty in the measurement of solvent activity was estimated to be ±0.0002.

Results and Discussions

Experimental Results. At isopiestic equilibrium, the activity of solvent in the reference and PPG solutions must be the same. Therefore, the isopiestic equilibrium mass

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Table 1. Densities and Refractive Indexes of the Solvents at 25 °C

	ρ/kg·m^{-3}		n_D	
solvent	exp	lit.	exp	lit.[c]
methanol	786.40	786.36[a]	1.3266	1.32652
ethanol	785.10	784.95[b]	1.3594	1.35941
2-propanol	781.22	780.98[b]	1.3753	1.3752
1-butanol	805.92	806.0[c]	1.3972	1.3973

[a] Reference 11. [b] Reference 12. [c] Reference 23.

fractions with reference standard solutions as reported in Tables 2−5 enabled the calculation of the solvent activity, a_1, in the solutions of alcohol (1) + PPG (2) from that of reference solutions. NaI was served as an isopiestic reference for each of the solutions of methanol, ethanol, or 2-propanol, because very accurate vapor pressure data are available for solutions of this salt in these solvents.[10−12] Similarly, since reliable activity data are available for solutions of $CaCl_2$ in 1-butanol,[13,14] this salt was chosen as an isopiestic reference for 1-butanol solutions. To calculate solvent activity for methanol, ethanol, and 2-propanol solutions, the following relations were used

$$\ln a_1 = -\nu m_{NaI}\Phi_{NaI}M_s, \quad m_{NaI} = \frac{w_{NaI}}{M_{NaI}(1 - w_{NaI})} \qquad (1a,b)$$

where υ is the sum of the stoichiometric numbers of anions and cations in the reference solutions and m_{NaI} and w_{NaI} are respectively the concentration (in mol·kg^{-1}) and mass fraction of NaI which is in isopiestic equilibrium with the polymer solutions. M_s and M_{NaI} are respectively the relative molar masses of the solvent and NaI, and Φ_{NaI} is the osmotic coefficient of the isopiestic reference standard, calculated at m_{NaI}. For methanol, ethanol, and 2-propanol solutions, the necessary Φ_{NaI} values at any m_{NaI} were obtained from the fitted Pitzer and Mayorga equation,[15] including the $\beta^{(2)}$ term as described in the previous papers.[15−17] For solutions of NaI in each of these solvents, it was shown that,[16−18] using the obtained Pitzer parameters, the osmotic coefficients, Φ_{NaI}, are reproducible with a standard deviation of 0.005. In the case of 1-butanol + PPG solutions, the isopiestic reference $CaCl_2$ in 1-butanol solution was used, for which instead of osmotic coefficients two sets of activity data have been reported.[13,14] However, examination of these two sets of data reveals that in the second report[14] the number of data points is more than that of the first measurements[13] and the quality of the second data set[14] is better than that of the first report. These activity data,[14] however, are represented to three decimal points; therefore, calculation of the corresponding osmotic coefficient data from these data with the help of eq 1a led to osmotic coefficient data with low accuracy. Hence, we decided to calculate the activity of solvent in1-butanol + $CaCl_2$ solutions at any 1-butanol mass fraction by fitting directly the activity data[14] to a suitable equation with respect to mass fraction of 1-butanol, w_1. It was found that the activity data are well fitted to a third-order polynomial

$$a_1 = b_0 w_1^{\ 3} + b_1 w_1^{\ 2} + b_2 w_1 + b_3 \qquad (2)$$

so that using the coefficients $b_0 = -24.2350$, $b_1 = 71.3810$, $b_2 = -68.0890$, and $b_3 = 21.9419$, the activity data for $CaCl_2$ in 1-butanol solutions, a_1, are reproducible with a standard deviation of about 0.001. Therefore, since the calculated activity data for the isopiestic reference are accurate to three decimal points, the solvent activity data reported in Table 5 for 1-butanol + PPG solutions are also given to three decimal points. However, since the isopiestic method is a relative method, from the tabulated isopiestic equilibrium molalities of Table 5, the values of a_1 can be easily recalculated as more accurate results become available for the reference standard.

Table 2. Experimental Isopiestic Mass Fractions *w*, Osmotic Coefficients Φ, and Activities of Methanol for Methanol (1) + PPG 1000 (2) at 25 °C

w_{NaI}	w_2[a]	Φ_{NaI}	a_1^{exp}	p^{exp}/kPa
0.0247	0.1802	0.833	0.9910	16.803
0.0267	0.1917	0.834	0.9903	16.791
0.0336	0.2170	0.837	0.9876	16.744
0.3892	0.2561	0.842	0.9855	16.708
0.0501	0.3078	0.854	0.9809	16.629
0.0595	0.3433	0.867	0.9768	16.559
0.0885	0.4276	0.915	0.9627	16.316
0.1152	0.5000	0.970	0.9474	16.053
0.1215	0.5144	0.983	0.9435	15.986
0.1628	0.5994	1.084	0.9137	15.475
0.1826	0.6410	1.136	0.8972	15.192
0.2095	0.6838	1.214	0.8715	14.751
0.2218	0.6991	1.251	0.8587	14.531
0.2442	0.7310	1.321	0.8332	14.095
0.2821	0.7776	1.448	0.7841	13.255
0.3190	0.8215	1.580	0.7288	12.310
0.3362	0.8427	1.644	0.7004	11.825
0.3965	0.8578	1.718	0.6664	11.246
0.3996	0.8909	1.887	0.5846	9.8540

[a] Polymer mass fraction.

Table 3. Experimental Isopiestic Mass Fractions *w*, Osmotic Coefficients Φ, and Activities of Ethanol for Ethanol (1) + PPG 1000 (2) at 25 °C

w_{NaI}	w_2	Φ_{NaI}	a_1^{exp}	p^{exp}/kPa
0.0106	0.0857	0.767	0.9950	7.831
0.0109	0.0910	0.766	0.9948	7.829
0.0125	0.1162	0.760	0.9941	7.824
0.0275	0.1968	0.734	0.9873	7.770
0.0358	0.2346	0.729	0.9845	7.748
0.0419	0.2667	0.727	0.9807	7.718
0.0483	0.2863	0.727	0.9770	7.689
0.0497	0.2873	0.727	0.9769	7.688
0.0603	0.3279	0.731	0.9716	7.647
0.0614	0.3303	0.731	0.9715	7.646
0.0670	0.3474	0.735	0.9681	7.619
0.0673	0.3494	0.735	0.9679	7.618
0.0736	0.3637	0.741	0.9645	7.591
0.0829	0.3915	0.751	0.9592	7.549
0.0988	0.4438	0.774	0.9493	7.471
0.1046	0.4579	0.784	0.9453	7.440
0.1170	0.4903	0.808	0.9363	7.369
0.1256	0.5106	0.827	0.9296	7.316
0.1317	0.5277	0.838	0.9258	7.286
0.1318	0.5285	0.842	0.9244	7.275
0.1608	0.5904	0.921	0.8972	7.061
0.1734	0.6194	0.960	0.8836	6.954
0.1928	0.6529	1.027	0.8594	6.763
0.2311	0.7265	1.161	0.8071	6.352

From the calculated solvent activity data, vapor pressures of the investigated solutions, p, were determined with the help of the following relation

$$\ln(a_1) = \ln\left(\frac{p}{p^*}\right) + \frac{(B - V_s^*)(p - p^*)}{RT} \qquad (3)$$

where B, V_s^*, and p^* are the second virial coefficient, molar volume, and vapor pressure of pure alcohol, respectively. The values of the physical properties of the solvents are summarized in Table 6. The experimental vapor pressure data are also given in Tables 2−5. In Table 5, the calculated vapor pressure data for 1-butanol + $CaCl_2$ solutions are given to two decimal points because the

Table 4. Experimental Isopiestic Mass Fractions w, Osmotic Coefficients Φ, and Activities of 2-Propanol for 2-Propanol (1) + PPG 1000 (2) at 25 °C

w_{NaI}	w_2	Φ_{NaI}	a_1^{exp}	p^{exp}/kPa
0.0133	0.0824	0.529	0.9943	5.744
0.0153	0.0934	0.527	0.9934	5.739
0.0191	0.1107	0.526	0.9921	5.731
0.0254	0.1506	0.528	0.9890	5.713
0.0291	0.1711	0.530	0.9874	5.704
0.0299	0.1729	0.530	0.9870	5.702
0.0375	0.2021	0.533	0.9835	5.681
0.0474	0.2373	0.535	0.9789	5.655
0.0550	0.2688	0.536	0.9753	5.634
0.0582	0.2925	0.537	0.9737	5.624
0.0696	0.3245	0.539	0.9682	5.592
0.0742	0.3377	0.540	0.9659	5.579
0.0784	0.3538	0.542	0.9638	5.567
0.0893	0.3924	0.546	0.9580	5.533
0.0986	0.4194	0.552	0.9527	5.502
0.1119	0.4491	0.564	0.9446	5.455
0.1174	0.4613	0.570	0.9410	5.434
0.1230	0.4729	0.577	0.9371	5.411
0.1222	0.4733	0.576	0.9377	5.415
0.1264	0.4824	0.582	0.9347	5.397
0.1315	0.5017	0.590	0.9309	5.375
0.1411	0.5198	0.607	0.9232	5.330
0.1485	0.5452	0.622	0.9167	5.293
0.1747	0.6073	0.693	0.8890	5.131
0.1870	0.6336	0.737	0.8730	5.038

Table 5. Experimental Isopiestic Mass Fractions w and Activities of Butanol for Butanol (1) + PPG 1000 (2) at 25 °C

w_{CaCl_2}	w_2	a_1^{exp}	p^{exp}/kPa	w_{CaCl_2}	w_2	a_1^{exp}	p^{exp}/kPa
0.0132	0.0977	0.985	0.81	0.1073	0.4785	0.835	0.69
0.0159	0.1135	0.982	0.81	0.1084	0.4802	0.833	0.69
0.0228	0.1576	0.974	0.80	0.1093	0.4868	0.831	0.68
0.0313	0.2231	0.964	0.79	0.1122	0.4915	0.824	0.68
0.0339	0.2364	0.961	0.79	0.1150	0.5031	0.817	0.67
0.0377	0.2439	0.956	0.79	0.1281	0.5383	0.784	0.65
0.0605	0.3252	0.924	0.76	0.1290	0.5425	0.781	0.64
0.0755	0.3748	0.899	0.74	0.1332	0.5521	0.770	0.63
0.0783	0.3865	0.894	0.74	0.1442	0.5833	0.738	0.61
0.0927	0.4336	0.867	0.71	0.1530	0.6110	0.710	0.59
0.0955	0.4431	0.861	0.71	0.1721	0.6482	0.643	0.53
0.1023	0.4653	0.847	0.70				

Table 6. Physical Properties of the Solvents

	$10^5 V_s^*$	$10^3 B$	$10^2 M_s$	p^*
solvent	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$kg \cdot mol^{-1}$	Pa
methanol[a]	4.0730	−2.075	3.2042	16957.7
ethanol[b]	5.8680	−2.981	4.6069	7870.3
2-propanol[b]	7.6920	−3.424	6.0067	5777.4
1-butanol[c]	9.1974	−4.750[d]	7.4124	823.9

[a] Reference 11. [b] Reference 12. [c] Reference 23. [d] The B value for 1-butanol was estimated by the method proposed by Tsonopoulos.[24]

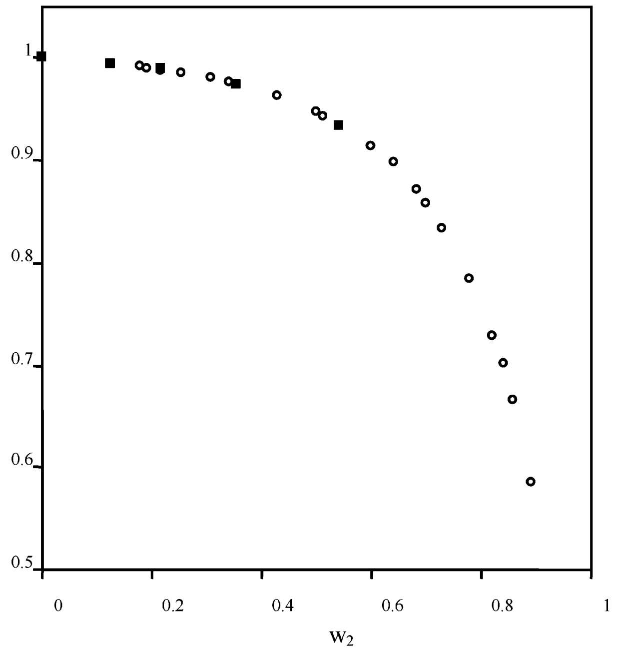

Figure 1. Comparison of measured methanol activity data for methanol (1) + PPG 1000 (2) solutions at 25 ° C: ○, this work for PPG of M_n = 976; ■, Lakhanpal et al.[2] for PPG of M_p = 1120.

Table 7. Parameters of Polynomial Equations along with the Corresponding Absolute Relative Percentage Deviations

system	c_0	c_1	c_2	c_3	ARD%(a_1)[a]
PPG + methanol	1.4440	−3.2092	2.3869	0.3870	0.95
PPG + ethanol	0.7277	−1.8530	1.6451	0.4828	0.15
PPG + 2-propanol	0.5449	−1.4362	1.3439	0.5488	0.09
PPG + 1-butanol	1.1870	−3.3617	3.3303	−0.1549	0.3

[a] ARD% = $100\sum_{i=1}^{n}|(a_1^{cal} - a_1^{exp})/a_1^{exp}|/n$, where n is the number of experimental data points.

corresponding activity data are meaningful to only three decimal points.

As shown in Figure 1 a comparison of the experimental methanol activity data can be made with the values obtained[2] for the methanol + PPG system with molar mass 1120, which is close to PPG 1000 considered in this work in respect to polymer molar mass. Figure 1 shows that there is a good agreement between our data and the literature.[2]

Correlation of Data

There are several models describing VLE of polymer solutions. Some authors use empirical equations. For instance, Eliassi et al.[19] have found that a cubic equation is sufficient for correlation of water activities in poly(ethylene) glycol + water systems. There are also theoretical models such as Flory−Huggins[4,5] and NRTL[20] models for correlation of solvent activity data for polymer solutions. In this work for correlation of solvent activity for the investigated systems, a cubic equation, the FH equation,[4] and the modified FH equation[5] with concentration dependent interaction parameters were considered.

The solvent activity data are fitted to a cubic equation

$$a_1 = c_0 w_1^3 + c_1 w_1^2 + c_2 w_1 + c_3 \tag{4}$$

with respect to solvent mass fraction, w_1. The coefficients of eq 4 along with its absolute relative percentage deviations (ARD%) are reported in Table 7.

The solvent activity data were also fitted to the model of Flory−Huggins,[4] which has the form

$$\ln a_1 = \ln \phi_1 + \left(1 - \frac{1}{r_2}\right)(1 - \phi_1) + \chi_{12}(1 - \phi_1)^2 \tag{5}$$

where φ_1 is the volume fraction of solvent and r_2 is the number of segments of polymer defined as the molar volume of polymer divided by the molar volume of solvent. χ_{12} is the interaction parameter of the system. For polymer solutions with different solvents, r_2 values were calculated using the relation $r_2 = (M_p/\rho_p)/(M_s/\rho_s)$, where ρ_p and ρ_s are the density of the polymer and the solvent, respectively. For the density of pure PPG 1000, the value ρ_p = 1005

Table 8. Parameters of Flory−Huggins and Modified Flory−Huggins Equations along with the Corresponding Absolute Relative Percentage Deviations

	conc range	Flory Huggins		modified Flory Huggins		
system	W_2	χ_{12}	ARD%(a_1)[a]	a	f	ARD%(a_1)
PPG + methanol	0.1802−0.8909	0.7656	2.76	0.4087	0.6096	0.35
PPG + ethanol	0.0857−0.7265	0.5408	0.59	0.3819	0.5352	0.09
PPG + 2-propanol	0.0824−0.6336	0.5368	0.36	0.4084	0.5060	0.07
PPG + 1-butanol	0.0977−0.6482	−0.0833	0.30	0.0227	1.4881	0.22

[a] ARD% = $100\sum_{i=1}^{n}|(a_1^{\mathrm{cal}} - a_1^{\mathrm{exp}})/a_1^{\mathrm{exp}}|/n$, where n is the number of experimental data points.

kg·m^{-3} given by the manufacturer was used. The obtained interaction parameters, χ_{12}, for the studied systems are presented in Table 8 along with the corresponding ARD% of the fit. On the basis of the obtained ARD%, we conclude that the FH equation[4] is a suitable model in representing our solvent activity data. Table 8 shows that the χ_{12} value decreases when the alcohol compound contains more and more of the methylene group. This can be explained as follows: methanol is the alcohol which has the strongest hydrogen bonding pattern; this prevents PPG from establishing strong intermolecular interactions with methanol leading to high values of the FH parameter. Then, with addition of a nonpolar methylene group, the self-association of the alcohol (ethanol, 2-propanol, and 1-butanol) will be decreased, leading to stronger interaction between the solvent and PPG; this is represented by lower values of the FH parameter. According to Flory−Huggins,[4] χ_{12} should be independent of concentration and molecular weight of the polymer. However, as pointed out by some authors,[16,17] in applying the FH equation to almost all polymer solutions, especially polar systems, it is necessary to consider χ_{12} dependent on concentration and molar mass of the polymer, in addition to temperature, to fit the activity data of components of the solution. Indeed, using eq 5, for each system considered in this work, we also obtain different χ_{12} values at different mass fractions of polymer. Therefore, we decided to consider the concentration dependency of χ_{12} in fitting the solvent activity data by using the equation proposed by Bae et al.[5] As shown previously,[9] at constant temperature (here, 25 °C), the Bae et al.[5] equation can be written as

$$\ln a_1 = \ln \phi_1 + \left(1 - \frac{1}{\mathrm{r}_2}\right)(1 - \phi_1) + \frac{d(1 - \phi_1)^2}{1 - f(1 - \phi_1)} \quad (6)$$

where d and f are adjustable parameters of the modified FH equation.[5] The results of fitting to eq 6 are also collected in Table 8. From the reported low ARD% with eq 6, we conclude that the quality of fitting with the modified FH equation[5] is better than that of the original FH equation. Furthermore, in correlation of solvent activity data for the studied systems, the modified FH equation[5] works better than the third-order polynomial (eq 4), which has more parameters.

In Figure 2, the measured solvent activity data for alcohol (1) + PPG 1000 (2) systems are shown together with the generated lines using the modified FH equation (eq 6) with the corresponding parameters reported in Table 8. As one can see from Figure 2, the modified FH model fit the data well. Also, the activities of alcohols tend to increase in the order 1-butanol > 2-propanol > ethanol > methanol.

Conclusions

Accurate activities of solvents in poly(propylene glycol) + methanol, ethanol, 2-propanol, and 1-butanol solutions have been measured by the isopiestic method at 25 °C. The results have been correlated to a cubic equation, the Flory-Huggins equation, and the modified Flory−Huggins equation. It was found that the Flory interaction parameter is strongly concentration dependent, so that the correlation of solvent activity data to the modified Flory−Huggins equation with concentration dependent parameters has resulted in lower absolute relative percentage deviations. Also, the modified FH equation works better than the third-order polynomial, which has more parameters.

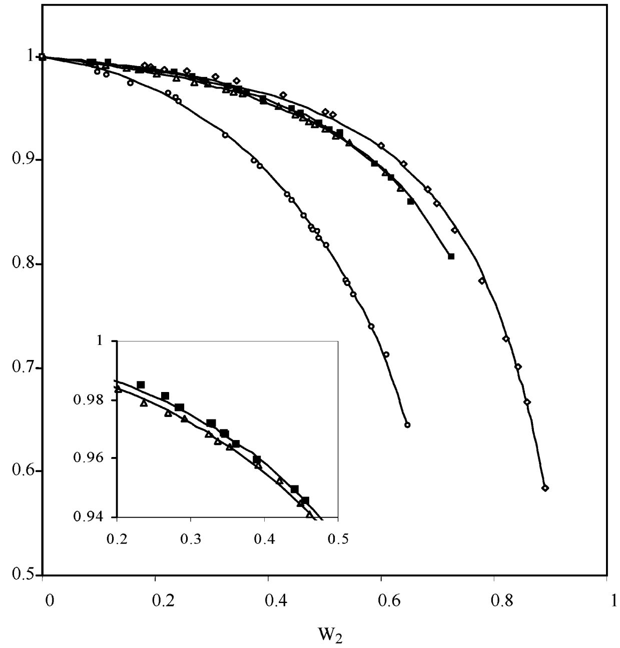

Figure 2. Solvent activity data for alcohol (1) + PPG 1000 at 25 ° C: ◇, methanol; ■, ethanol; △, 2-propanol; ○, 1-butanol. Lines were generated from fitting of the experimental activity data to the modified Flory−Huggins model.[5]

List of Symbols

a_1 = solvent activity
a_1^{exp} = experimental solvent activity
b_0, b_1, b_2, and b_3 = coefficients of eq 2
B = second virial coefficient
c_0, c_1, c_2, and c_3 = coefficients of eq 4
d, f = adjustable parameters of the modified FH equation
m_{NaI} = NaI concentration (mol·kg^{-1})
M_{s} = molar mass of solvent (kg·mol^{-1})
M_{p} = molar mass of polymer (kg·mol^{-1})
M_{NaI} = molar mass of NaI (kg·mol^{-1})
n_{D} = solvent refractive index
p = vapor pressure of polymer solution (kPa)
p^* = vapor pressure of pure solvent (Pa)
p^{exp} = experimental vapor pressure of polymer solution (kPa)
r_2 = the number of segments of polymer

R = gas constant
T = temperature (K)
V_s^* = molar volume of pure solvent
w_1 = mass fraction of solvent
w_2 = mass fraction of polymer
w_{CaCl_2} = mass fraction of $CaCl_2$
w_{NaI} = mass fraction of NaI

Greek Letters

$\beta^{(2)}$ = Pitzer ionic interaction parameter
Φ_{NaI} = osmotic coefficient of the isopiestic reference standard
φ_1 = volume fraction of solvent
υ = sum of stoichiometric numbers of anions and cations in the reference solutions
ρ_p = density of the polymer ($kg \cdot m^{-3}$)
ρ_s = density of solvent ($kg \cdot m^{-3}$)
χ_{12} = Flory interaction parameter

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