Measurement and Correlation of Phase Equilibria for Poly(propylene glycol) 400 + Ethanol and + 2-Propanol Systems at Different Temperatures

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The activities of ethanol and 2-propanol in poly(propylene glycol) 400 (PPG 400) solutions have been measured by the improved isopiestic method at $T = (298.15 \text{ to } 328.15)$ K. The original equation of Flory−Huggins and the modified Flory−Huggins equation with concentration-dependent interaction parameters have been used for the correlation of the experimental solvent activity data. It was found that for the studied systems at any mass fraction, as the temperature is increased the solvent activities and Flory parameters are both decreased, indicating an increase of interaction between polymer and solvents as the temperature is increased. The reliability of the two local composition models, NRTL and Wilson, was also assessed by fitting the experimental activity data to these models. All of these models satisfactorily present the obtained experimental activity data at different temperatures.

Introduction

In recent years, numerous studies have been carried out on mixtures containing poly(propylene glycols) (PPGs). PPG is used in many formulations for polyurethanes. It is used as a rheology modifier;[1] in solid tires, automobile seats,[2] foams,[3] membranes;[4] and in talc separation from talc-carbonate ore.[5] An understanding of the thermodynamics of the polymer solutions is important in practical applications such as polymerizations, devolatilization, and incorporation of plasticizers and other additives. Diffusion phenomena in polymer melts and solutions are strongly affected by nonideal solution behavior since the chemical potential rather than the concentration provides the driving force for diffusion. Proper design and engineering of many polymer processes depend greatly upon accurate modeling of thermodynamic parameters such as solvent activities.

The vapor−liquid data have been compiled by Wohlfarth[6] for some polymer + solvent systems. In regard to PPG + alcohol solutions, few vapor pressure data for the PPG + methanol system with polymer of molar masses 150, 1120, 1955, and 3350 have been measured[7] at $T = (248.15 \text{ to } 298.15)$ K. Vapor−liquid equilibria data of some binary alcohol + PPG were measured[8,9] by an apparatus based on the principle of electromicrobalance. Tested alcohols were methanol, ethanol, and 1-propanol with polymer of molar masses 2000 and 400. In their vapor sorption measurements,[9] however, they only considered the methanol, ethanol, and 1-propanol mass fractions in the limited ranges of 0.0354 to 0.1693, 0.0282 to 0.1320, and 0.0246 to 0.2354, respectively, for PPG400 at 303.15 K. In a similar work, Kim et al.[8] reported the above alcohol activity data for solutions of PPG2000 in the alcohol with alcohol mass fractions of about 0.01 to 0.33. Alcohol activity data in PPG + methanol, + ethanol, + 2-propanol, and 1-butanol solutions of PPG with molar mass of 1000 is available[10] at only 298.15 K.

This work is the continuation of our study[11] on the thermodynamics of polymer + solvent systems at different temperatures. In the present report, activities of ethanol and 2-propanol in solutions of PPG having a molar mass of 400 are measured by the improved isopiestic method at $T = (298.15 \text{ to } 328.15)$ K. As far as we know there is no vapor pressure or activity data for PPG400 + ethanol or + 2-propanol systems at different temperatures in the literature. The recent vapor pressure measurements on the solutions of LiBr in ethanol[12] and 2-propanol[13] provide us the osmotic coefficients of these solutions in wide ranges of concentrations and at different temperatures. These osmotic coefficient data permit us to use LiBr in ethanol and 2-propanol systems as an isopiestic standard; therefore, isopiestic measurement is now possible at higher concentrations and temperatures for solutions of other salts or polymers in solvents than was possible before. The obtained solvent activity data for ethanol + PPG400 and 2-propanol + PPG400 systems at different temperatures were fitted to the Flory−Huggins[14,15] and two local composition models, NRTL[16] and Wilson.[17]

Experimental Procedures

Materials. All the chemicals were obtained from Merck. Lithium bromide with purity of minimum mass fraction 0.995 was dried in an electrical oven at about 110 °C for 24 h prior to use. Ethanol and 2-propanol with purity of minimum mass fraction 0.995 was dehydrated according to Vogel.[18] Double-distilled, deionized water was used. For molar mass of PPG, the value 400 g·mol^{-1} was used.

Apparatus and Procedures. The isopiestic apparatus employed is essentially similar to the one used previously.[19] Recently this technique has been used for the measurement of activity of the solvent in alcohol + poly(vinylpyrrolidone) (PVP),[20] alcohol + poly(propylene glycol) (PPG),[10] and 2-propanol + poly(ethylene glycol) (PEG)[21] at 298.15 K and methanol + PEG[11] systems at (298.15 to 328.15) K. This apparatus consisted of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard LiBr solutions, two flasks contained PPG solutions, and the central flask was used as a solvent reservoir. The apparatus was held in a constant temperature bath at least 120 h for equilibration at $T = (298.15 \text{ to } 328.18)$ K. The temperature was controlled to within ± 0.005 °C by a Heto temperature controller (Hetotherm PF, Heto Lab

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Table 1. Experimental Isopiestic Mass Fraction *w*, Osmotic Coefficients Φ, and Ethanol Activity a_1 for Ethanol (1) + PPG400 (2) at Different Temperatures

w_{LiBr}	w_2	Φ_{LiBr}	a_1	p/kPa	w_{LiBr}	w_2	Φ_{LiBr}	a_1	p/kPa	w_{LiBr}	w_2	Φ_{LiBr}	a_1	p/kPa
T = 298.15 K														
0.0143	0.0919	0.759	0.9883	7.781	0.0693	0.3460	0.827	0.9364	7.369	0.1414	0.6146	1.192	0.8119	6.382
0.0169	0.1117	0.755	0.9863	7.765	0.0715	0.3559	0.832	0.9343	7.352	0.1426	0.6177	1.202	0.8089	6.358
0.0217	0.1294	0.753	0.9824	7.734	0.0785	0.3845	0.855	0.9257	7.284	0.1503	0.6431	1.263	0.7889	6.200
0.0259	0.1508	0.752	0.9790	7.707	0.0843	0.4064	0.875	0.9180	7.223	0.1652	0.6877	1.397	0.7457	5.858
0.0316	0.1806	0.755	0.9742	7.669	0.0913	0.4329	0.903	0.9082	7.145	0.1737	0.7166	1.483	0.7183	5.641
0.0345	0.1958	0.758	0.9717	7.649	0.0991	0.4655	0.937	0.8964	7.051	0.1846	0.7460	1.603	0.6804	5.342
0.0369	0.2133	0.760	0.9695	7.632	0.1055	0.4876	0.968	0.8860	6.969	0.2056	0.8001	1.868	0.5987	4.697
0.0542	0.2825	0.788	0.9533	7.503	0.1177	0.5326	1.034	0.8639	6.794	0.2113	0.8188	1.950	0.5745	4.506
0.0599	0.3066	0.801	0.9474	7.456	0.1298	0.5749	1.110	0.8389	6.596	0.2184	0.8322	2.056	0.5437	4.263
T = 308.15 K														
0.0180	0.1123	0.722	0.9860	13.556	0.0680	0.3350	0.819	0.9386	12.897	0.1628	0.6752	1.361	0.7550	10.350
0.0239	0.1291	0.727	0.9813	13.491	0.0864	0.4050	0.882	0.9153	12.573	0.1795	0.7260	1.527	0.7015	9.610
0.0306	0.1702	0.736	0.9757	13.413	0.0933	0.4322	0.910	0.9054	12.435	0.1876	0.7460	1.616	0.6730	9.217
0.0368	0.2001	0.746	0.9702	13.336	0.1020	0.4671	0.948	0.8921	12.251	0.1982	0.7755	1.743	0.6332	8.667
0.0393	0.2171	0.750	0.9680	13.306	0.1086	0.4925	0.981	0.8810	12.097	0.1981	0.7763	1.743	0.6333	8.669
0.0492	0.2587	0.770	0.9586	13.175	0.1157	0.5196	1.08	0.8683	11.920	0.2023	0.7875	1.798	0.6164	8.435
0.0530	0.2757	0.779	0.9548	13.122	0.1248	0.5486	1.072	0.8503	11.671	0.2114	0.8088	1.921	0.5791	7.921
0.0616	0.3079	0.801	0.9458	12.997	0.1530	0.6444	1.275	0.7833	10.742	0.2150	0.8156	1.973	0.5637	7.709
T = 318.15 K														
0.0216	0.1175	0.715	0.9834	22.653	0.0944	0.4322	0.904	0.9049	20.818	0.1805	0.7170	1.500	0.7043	16.149
0.0312	0.1580	0.728	0.9754	22.466	0.1042	0.4678	0.947	0.8897	20.463	0.2003	0.7712	1.724	0.6325	14.485
0.0373	0.1996	0.738	0.9702	22.344	0.1085	0.4818	0.967	0.8826	20.297	0.2043	0.7822	1.774	0.6166	14.118
0.0444	0.2368	0.752	0.9636	22.190	0.1145	0.5038	0.998	0.8720	20.050	0.2071	0.7880	1.811	0.6053	13.856
0.0656	0.3174	0.804	0.9419	21.682	0.1268	0.5455	1.068	0.8482	19.495	0.2184	0.8152	1.964	0.5586	12.777
0.0702	0.3382	0.817	0.9367	21.561	0.1338	0.5726	1.112	0.8334	19.150	0.2227	0.8269	2.025	0.5403	12.355
0.0858	0.3939	0.870	0.9170	21.100	0.1546	0.6438	1.264	0.7826	17.968					
0.0875	0.3979	0.870	0.9169	21.098	0.1607	0.6516	1.314	0.7658	17.577					
T = 328.15 K														
0.0236	0.1200	0.726	0.9815	36.596	0.0824	0.3842	0.868	0.9207	34.284	0.1578	0.6391	1.293	0.7734	28.707
0.0248	0.1293	0.728	0.9805	36.558	0.0871	0.3978	0.885	0.9143	34.041	0.1584	0.6454	1.298	0.7715	28.635
0.0377	0.1940	0.748	0.9694	36.135	0.0965	0.4325	0.923	0.9007	33.524	0.1856	0.7124	1.549	0.6875	25.471
0.0408	0.2126	0.754	0.9665	36.025	0.1017	0.4555	0.945	0.8927	33.221	0.1916	0.7366	1.614	0.6662	24.671
0.0447	0.2298	0.762	0.9629	35.888	0.1084	0.4829	0.977	0.8815	32.796	0.2060	0.7729	1.782	0.6124	22.652
0.0519	0.2490	0.778	0.9558	35.618	0.1168	0.5018	1.020	0.8665	32.228	0.2150	0.7944	1.897	0.5762	21.297
0.0626	0.3054	0.806	0.9445	35.188	0.1277	0.5427	1.082	0.8453	31.425	0.2209	0.8077	1.978	0.5515	20.373
0.0698	0.3329	0.827	0.9363	34.876	0.1300	0.5548	1.096	0.8404	31.239	0.2262	0.8200	2.055	0.5287	19.521

Equipment, Denmark). After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance (Shimatzu, 321-34553, Shimatzu Co., Japan) with an uncertainty of $\pm 1 \times 10^{-7}$ kg. 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 Discussion

Experimental Results. At isopiestic equilibrium, the activity of solvent in the reference and PPG solutions must be the same. Therefore, the isopiestic equilibrium mass fractions with reference standard solutions of LiBr in ethanol and 2-propanol as reported in Tables 1 and 2, respectively, enabled the calculation of the solvent activity (a_1) in the solutions of ethanol (1) + PPG (2) and 2-propanol (1) + PPG (2) from that of reference solutions using the relations

$$\ln a_1 = -\upsilon m_{LiBr}\phi_{LiBr}M_S \tag{1a}$$

$$m_{LiBr} = \frac{w_{LiBr}}{M_{LiBr}(1 - w_{LiBr})} \tag{1b}$$

where υ is the sum of stoichiometric numbers of anion and the cation in the reference solutions; m_{LiBr} and w_{LiBr} are respectively the substance concentration and mass fraction of LiBr, which is in isopiestic equilibrium with the polymer solutions; M_s and M_{LiBr} are respectively the molar masses of the solvent and LiBr; and ϕ_{LiBr} is the osmotic coefficient of the isopiestic reference standard, calculated at m_{LiBr}. The necessary ϕ_{LiBr} values at any m_{LiBr} were obtained from the fitted extended Pitzer ion interaction model of the Archer equation:

$$\phi_{LiBr} = \left[1 - A_\phi\left(\frac{\sqrt{m_{LiBr}}}{1 + b\sqrt{m_{LiBr}}}\right)\right] + m_{LiBr}(\beta^{(0)} + \beta^{(1)}\exp[-\alpha_1\sqrt{m_{LiBr}}] + \beta^{(2)}\exp[-\alpha_2\sqrt{m_{LiBr}}]) + (m_{LiBr})^2(C^{(0)} + C^{(1)}\exp[-\alpha_3\sqrt{I}]) \tag{2}$$

The parameters of eq 2 for LiBr in ethanol and 2-propanol solutions in the concentration ranges of (0.0705 to 3.4451) mol·kg^{-1} and (0.0743 to 1.4825) mol·kg^{-1}, respectively, and temperature ranges of T = (298.15 to 333.15) K have been reported by Nasirzadeh et al.[12,13] It was also shown that[12,13] using $\alpha_1 = 2$, $\alpha_2 = 7$, $\alpha_3 = 1$, and $b = 3.2$, the osmotic coefficients ϕ_{LiBr} are reproducible with standard deviation of about 0.01 in the above concentration and temperature ranges. The obtained ethanol and 2-propanol activity data for the systems ethanol (1) + PPG400 (2) and 2-propanol (1) + PPG400 (2) are given in Tables 1 and 2, respectively. To see the effect of temperature on the solvents activity, the a_1 values of ethanol were plotted versus polymer mass fractions at (298.15 and 328.15) K in Figure 1, as an example. The experimental activity data for ethanol solutions of PPG400 obtained by Jung et al.[9] using electromicrobalance apparatus at 303.15 K are also shown in

Table 2. Experimental Isopiestic Mass Fraction w, Osmotic Coefficients Φ, and 2-Propanol Activity a_1 for 2-Propanol (1) + PPG400 (2) at Different Temperatures

w_{LiBr}	w_2	Φ_{LiBr}	a_1	p/kPa	w_{LiBr}	w_2	Φ_{LiBr}	a_1	p/kPa	w_{LiBr}	w_2	Φ_{LiBr}	a_1	p/kPa
							T = 298.15 K							
0.0245	0.1098	0.500	0.9827	5.779	0.0655	0.2582	0.516	0.9512	5.495	0.1023	0.4021	0.642	0.9037	5.219
0.0259	0.1152	0.499	0.9818	5.678	0.0675	0.2647	0.520	0.9492	5.484	0.1061	0.4139	0.657	0.8977	5.184
0.0308	0.1381	0.496	0.9784	5.673	0.0760	0.2989	0.543	0.9401	5.431	0.1184	0.4626	0.710	0.8764	5.061
0.0374	0.1600	0.493	0.9738	5.653	0.0803	0.3142	0.556	0.9349	5.400	0.1237	0.4806	0.731	0.8670	5.006
0.0465	0.1857	0.492	0.9673	5.627	0.0911	0.3573	0.595	0.9207	5.318	0.1365	0.5366	0.776	0.8438	4.871
0.0579	0.2284	0.502	0.9582	5.589	0.0947	0.3707	0.610	0.9154	5.287	0.1390	0.5436	0.784	0.8393	4.845
							T = 308.15 K							
0.0188	0.0844	0.485	0.9872	10.347	0.0542	0.2129	0.498	0.9608	10.067	0.1107	0.4217	0.675	0.8903	9.321
0.0200	0.0913	0.485	0.9864	10.339	0.0551	0.2141	0.498	0.9606	10.065	0.1114	0.4265	0.678	0.8891	9.308
0.0236	0.1014	0.487	0.9839	10.312	0.0614	0.2394	0.507	0.9552	10.008	0.1132	0.4338	0.687	0.8858	9.273
0.0291	0.1236	0.488	0.9800	10.271	0.0751	0.2843	0.537	0.9414	9.862	0.1180	0.4524	0.709	0.8770	9.180
0.0336	0.1362	0.488	0.9768	10.237	0.0843	0.3226	0.566	0.9304	9.745	0.1232	0.4764	0.735	0.8668	9.072
0.0358	0.1480	0.488	0.9752	10.220	0.0854	0.3252	0.569	0.9292	9.733	0.1260	0.4861	0.749	0.8612	9.013
0.0426	0.1686	0.490	0.9703	10.168	0.0948	0.3625	0.605	0.9161	9.594	0.1282	0.4960	0.759	0.8568	8.967
0.0508	0.1982	0.494	0.9641	10.102	0.1020	0.3882	0.635	0.9050	9.477	0.1341	0.5215	0.787	0.8447	8.839
							T = 318.15 K							
0.0180	0.0752	0.467	0.9882	17.938	0.0585	0.2184	0.501	0.9579	17.381	0.0940	0.3514	0.595	0.9181	16.650
0.0219	0.0942	0.469	0.9856	17.890	0.0629	0.2379	0.509	0.9539	17.307	0.1006	0.3767	0.618	0.9088	16.479
0.0262	0.0998	0.472	0.9826	17.835	0.0693	0.2597	0.522	0.9476	17.192	0.1079	0.4015	0.644	0.8979	16.279
0.0371	0.1459	0.478	0.9748	17.692	0.0740	0.2738	0.534	0.9427	17.102	0.1112	0.4118	0.655	0.8928	16.186
0.0462	0.1748	0.485	0.9680	17.567	0.0811	0.3042	0.553	0.9347	16.955	0.1154	0.4312	0.670	0.8860	16.061
0.0502	0.1898	0.489	0.9649	17.510	0.0876	0.3268	0.574	0.9266	16.806	0.1247	0.4636	0.701	0.8709	15.784
							T = 328.15 K							
0.0321	0.1220	0.474	0.9785	29.594	0.0621	0.2303	0.499	0.9553	28.880	0.1110	0.4051	0.651	0.8935	26.982
0.0370	0.1416	0.477	0.9749	29.483	0.0714	0.2608	0.516	0.9466	28.613	0.1212	0.4492	0.700	0.8749	26.411
0.0430	0.1623	0.480	0.9706	29.351	0.0799	0.2780	0.537	0.9376	28.336	0.1271	0.4678	0.730	0.8632	26.053
0.0482	0.1798	0.484	0.9667	29.231	0.0830	0.3055	0.546	0.9338	28.219	0.1297	0.4862	0.743	0.8579	25.890
0.0560	0.2043	0.491	0.9605	29.040	0.0888	0.3218	0.564	0.9268	28.004	0.1375	0.5139	0.784	0.8411	25.375
0.0590	0.2138	0.495	0.9580	28.963	0.1049	0.3740	0.625	0.9036	27.292	0.1427	0.5248	0.812	0.8294	25.017

Table 3. Physical Properties of Ethanol[a] and 2-Propanol[b]

T/K	$10^5 V^*_s$/m^3·mol^{-1}	$10^3 B$/m^3·mol^{-1}	ρ/kg· m^{-3}	p^*/kPa
		Ethanol		
298.15	5.869	−2.8357	783.365	7.874
308.15	5.935	−2.2570	775.231	13.751
318.15	6.005	−1.8259	767.097	23.042
328.15	6.078	−1.5007	758.963	37.301
		2-Propanol		
298.15	7.808	−2.7668	780.766	5.779
308.15	7.895	−2.2282	772.138	10.483
318.15	7.988	−1.8265	763.177	18.155
328.15	8.087	−1.5226	758.559	30.256

[a] Taken from ref 12. [b] Taken from ref 13.

Table 4. Flory Parameters Calculated from Equation 4 along with the Standard Deviations for Ethanol and 2-Propanol Activity σ (a_1) for the Systems Ethanol (1) + PPG400 (2) and 2-Propanol (1) + PPG400 (2) at Different Temperatures

T/K	χ	$\sigma(a_1)$	T/K	χ	σ (a_1)
		Ethanol + PPG400			
298.15	0.4443	0.0064	318.15	0.3998	0.0060
308.15	0.4205	0.0055	328.15	0.3424	0.0028
		2-Propanol + PPG400			
298.15	0.3779	0.0017	318.15	0.3074	0.0006
308.15	0.3338	0.0010	328.15	0.2860	0.0015

Figure 1. As can be seen from Figure 1, for a given polymer mass fraction, an increase in temperature causes a slight decrease in their activity values. Similar behavior is observed for the 2-propanol + PPG system.

From the calculated solvent activity data, the vapor pressure of ethanol and 2-propanol solutions (p) were determined with the help of the following relation

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

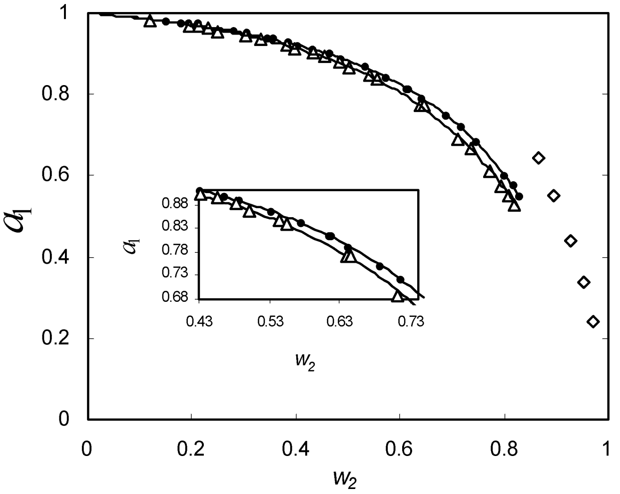

Figure 1. Experimental and calculated activity of ethanol (a_1) plotted against mass fraction of polymer (w_2), for ethanol (1) + PPG400 (2) system at two temperatures: ●, 298.15 K; Δ, 328.15 K; −, modified Flory−Huggins model (eq 5); ◇, experimental activities at 303.15 K taken from ref 10.

where B, V_s* and p* are the second virial coefficient, molar volume, and vapor pressure of pure solvents, respectively. The values of the physical properties for the ethanol and 2-propanol, which are taken from Nasirzadeh et al.,[12,13] are summarized in Table 3. The experimental vapor pressure data are also given in Tables 1 and 2.

In Figure 2, the ethanol and 2-propanol activities are compared as an example at 298.15 K. For the investigated systems, in Figure 3 the activity of ethanol obtained in this work at 298.15 K are compared with our previous work[10] in which the molar mass of PPG was chosen to be 1000. As can be seen from Figure 3, in the same polymer mass fraction the magnitude of the solvent activities have the order of PPG1000 > PPG400.

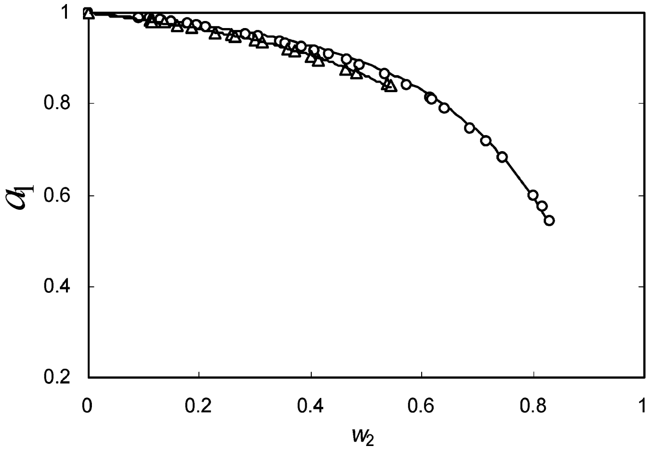

Figure 2. Experimental and calculated activity of ethanol and 2-propanol (a_1) plotted against mass fraction of polymer (w_2) at 298.15 K: ○, ethanol (1) + PPG400 (2); Δ, 2-propanol (1) + PPG400 systems; —, Flory−Huggins model (eq 4).

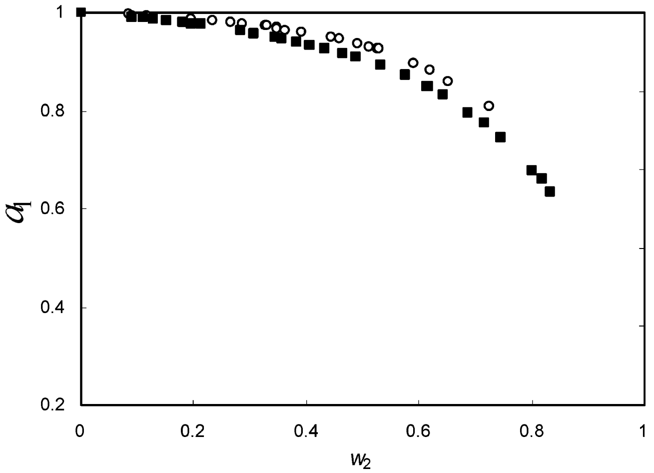

Figure 3. Experimental activity of ethanol (a_1) plotted against mass fraction of polymer (w_2) at 298.15 K: ○, ethanol (1) + PPG1000 (2); ■, ethanol (1) + PPG400.

Similar behavior is observed for PPG + 2-propanol system with two different molar masses of 400 and 1000. In fact the solvent absorption of a polymer increases with a decrease in the molar mass of the polymer. This behavior is also observed for solutions of PPG, PEG, and PVP in acetonitrile.[22]

Correlation of Data. Solvents activity values a_1 at each temperature reported in Table 1 and 2 were fitted to the original Flory−Huggins model,[14] which has the following form:

$$\ln a_1 = \ln z_1 + \left(1 - \frac{1}{r_2}\right)(1 - z_1) + \chi\,(1 - z_1)^2 \qquad (4a)$$

$$z_i = \frac{r_i n_i}{r_1 n_1 + r_2 n_2} \qquad (4b)$$

In eq 4, χ is the Flory parameter; z_i, n_i, and x_i are respectively the volume fraction, the number moles, and the mole fraction of the component i; and r_i is the number of segment in the component i.

The result of the fitting to eq 4 is given in Table 4. The standard deviations σ (a_1) given in Table 4 indicates that eq 4 represents the experimental solvent activity data fairly well. For both systems the χ value reported in Table 4 decreases as the temperature increases. This decreasing of the χ value indicates that as the temperature increases the interaction between PPG and solvents become stronger. However, since there is a little difference between the obtained χ values, the temperature has only small effect on the interaction between PPG and solvents. Similar result has been obtained for PEG400 + methanol system at different tempratures.[11]

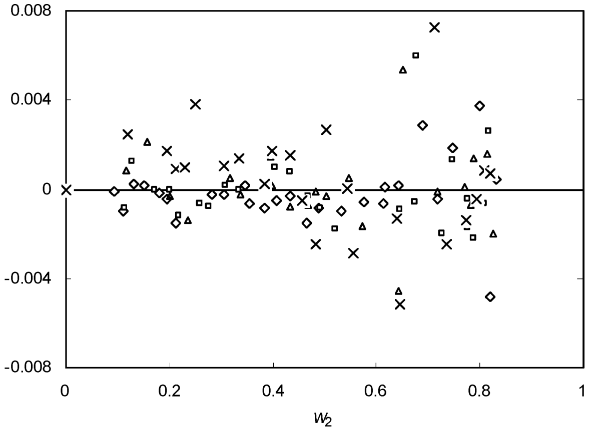

Figure 4. Difference between the experimental and calculated ethanol activities with the modified Flory−Huggins model (eq 5) at different temperatures: ◇, 298.15 K; □, 308.15 K; Δ, 318.15 K; ×, 328.15 K.

Table 5. Flory Parameters Calculated from Equation 5 along with the Standard Deviations for Ethanol and 2-Propanol Activity σ (a_1) for the Systems Ethanol (1) + PPG400 (2) and 2-Propanol (1) + PPG400 (2) at Different Temperatures

T/K	d_0	d_1	d_2	f	σ (a_1)
			Ethanol + PPG400		
	4.4748	0.6054	−0.7260	0.3549	
298.15					0.0021
308.15					0.0017
318.15					0.0036
328.15					0.0038
			2-Propanol + PPG400		
	4.5547	1.0865	−0.7438	0.3435	
298.15					0.0017
308.15					0.0013
318.15					0.0007
328.15					0.0015

The dependence of the Flory parameter on concentration and temperature, however, should be considered. The following modified Flory−Huggins equation

$$\ln a_1 = \ln z + \left(1 - \frac{1}{r_2}\right)(1 - z) + \left[\frac{d_0}{1 - f(1 - z)} + \frac{d_1}{T[1 - f(1 - z)]} + \frac{d_2 \ln T}{1 - f(1 - z)}\right](1 - z)^2 \qquad (5)$$

given by Bae et al.[15] was known to be the successful in representing the concentration as well as temperature dependency of the solvent activity data in binary polymer + solvent systems. Therefore, we also fitted the experimental ethanol and 2-propanol activity data of Tables 1 and 2 to eq 5. The obtained parameters d_0, d_1, d_2, and f and standard deviation σ (a_1) are reported in Table 5. To see the performance of eq 5 in representing solvent activity data, as an example, the lines generated for ethanol activities at (298.15 and 328.15) K were obtained using the parameters of eq 5. These are also shown in Figure 1. The difference between the experimental and calculated solvent activities with the modified Flory−Huggins model (eq 5) are shown at different temperatures in Figures 4 and 5 for solutions of ethanol and 2-propanol in PPG, respectively.

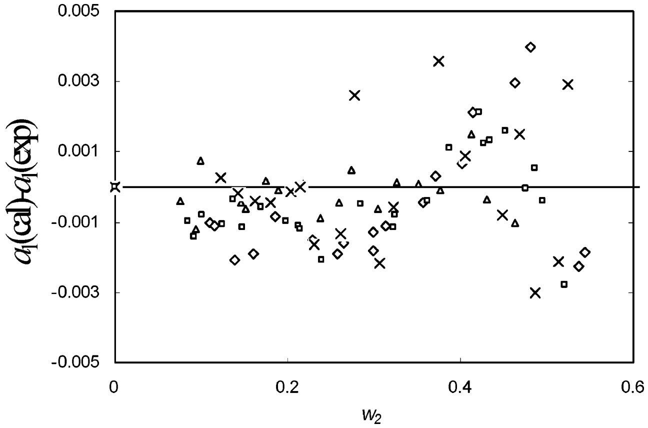

Figure 5. Difference between the experimental and calculated 2-propanol activities with the modified Flory−Huggins model (eq 5) at different temperatures: ◇, 298.15 K; □, 308.15 K; Δ, 318.15 K; ×, 328.15 K.

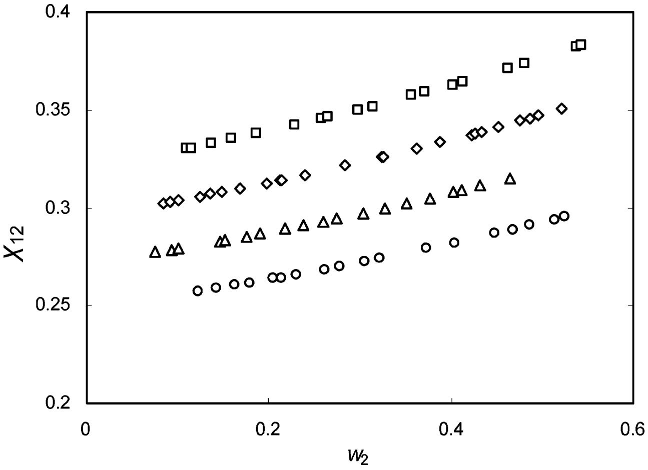

Figure 6. Variation of the Flory parameter χ_{12} with concentration and temperature for 2-propanol (1) + PPG400 (2) system: □, 298.15 K; ◇, 308.15 K: Δ, 318.15 K: ○, 328.15 K.

In the modified Flory−Huggins model, the Flory−Huggins parameter χ_{12} is defined as

$$\chi_{12}(T,z) = \frac{d_0}{1 - f(1 - z)} + \frac{d_1}{T[1 - f(1 - z)]} + \frac{d_2 \ln T}{1 - f(1 - z)} \tag{6}$$

The variation of the Flory−Huggins parameter χ_{12} with PPG mass fraction and the temperature were obtained from eq 6. The corresponding plot is shown in Figure 6 for 2-propanol as an example. Figure 6 shows that for this system the modified Flory−Huggins model gives the χ_{12} values, which decrease by increase in temperature, similar to the trend obtained by the original Flory−Huggins model as reported in Table 4. Similar behavior is observed for the ethanol + PPG system.

As an example, in Figure 2 the measured solvent activity data for PPG400 + ethanol and PPG400 + 2-propanol systems at 298.15 K are shown together with the generated lines using the Flory−Huggins model (eq 4) with the corresponding parameters reported in Table 4. As one can see from Figure 2, activities of alcohols tend to increase in the order ethanol > 2-propanol. This behavior is consistent with the values of Flory parameters reported in Table 4 in that at each temperature χ values decreases from ethanol to 2-propanol, indicating a stronger interaction of 2-propanol than ethanol with PPG400. This trend was also observed for solutions of these alcohols with PVP[20] and PEG methacrylate at 298.15 K.[23]

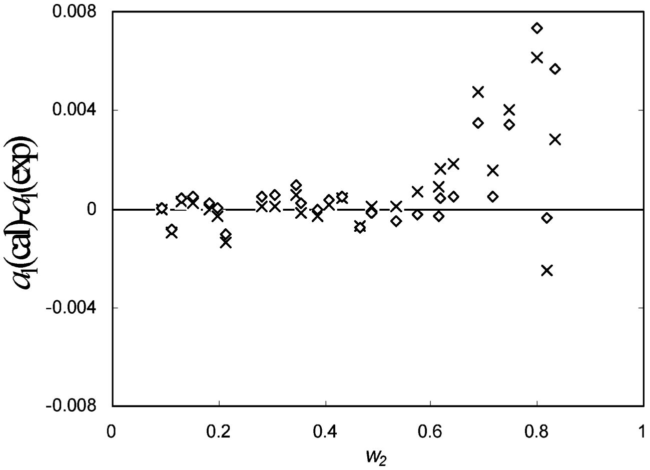

Figure 7. Difference between the experimental and calculated ethanol activities with the NRTL and Wilson models (eqs 8 to 12) at 298.15 K: ◇, NRTL; ×, Wilson.

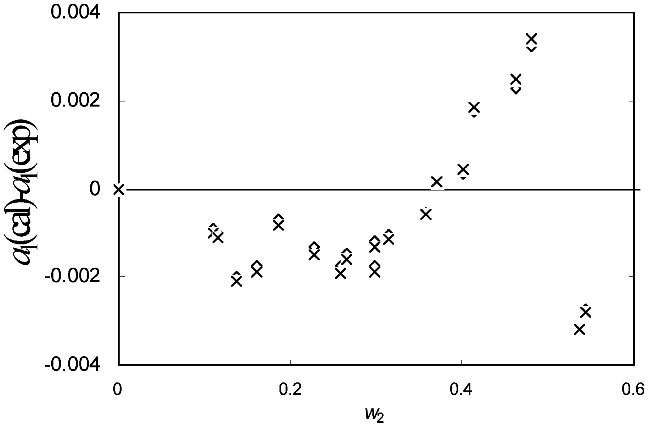

Figure 8. Difference between the experimental and calculated 2-propanol activities with the NRTL and Wilson models (eqs 8 to 12) at 298.15 K: ◇, NRTL; ×, Wilson.

For the correlation of experimental solvent activity data for the investigated systems, the two local composition models (NRTL and Wilson) were also considered. In these models, the activity coefficient of the solvent (1) is considered as the sum of the combinatorial, $\ln \gamma_1^{\text{Comb}}$, and the residual contribution, $\ln \gamma_1^{\text{Res}}$:

$$\ln \gamma_1 = \ln \gamma_1^{\text{Comb}} + \ln \gamma_1^{\text{Res}} \tag{7}$$

In this work, for these local composition models the Freed correction to the Flory−Huggins expression[24] was used for the combinatorial contribution, and the NRTL and Wilson models were used for the residual contribution.

The Freed Flory−Huggins combinatorial term is the exact solution for the Flory−Huggins lattice theory. It is expressed as a polynomial expansion in the first-order correction:

$$\ln \gamma_1^{\text{Comb}} = \ln\frac{z_1}{x_1} + \left(1 - \frac{r_1}{r_2}\right)z_2 + \alpha\left(\frac{1}{r_1} - \frac{1}{r_2}\right)^2 {z_2}^2 \tag{8}$$

where the first and second terms on the right-hand side of eq 8 account for the contribution for the excess entropy associated with random mixing and are the same as the expression in Flory−Huggins theory. The third term is the correction to the Flory−Huggins theory and may be understood

Table 6. NRTL and Wilson Parameters Calculated from Equations 7 and 8 along with the Standard Deviations for Ethanol and 2-Propanol Activity σ (a_1) for the Systems Ethanol (1) + PPG400 (2) and 2-Propanol (1) + PPG400 (2) at Different Temperatures

		NRTL				Wilson			
system	T/K	$a_w^{(1)}$	$a_s^{(1)}$	$a^{(2)}$	σ (a_1)	$a_w^{(1)} \times 10^{-4}$	$a_s^{(1)} \times 10^{-4}$	$a^{(2)} \times 10^{-4}$	σ (a_1)
ethanol (1) + PPG400 (2)		−0.9941	0.3773	0.5157		−0.8264	0.6354	0.1857	
	298.15				0.0019				0.0017
	308.15				0.0017				0.0018
	318.15				0.0036				0.0036
	328.15				0.0035				0.0035
2-propanol (1) + PPG400 (2)		−1.0038	0.2082	0.5843		−0.7745	0.5359	0.1974	
	298.15				0.0017				0.0017
	308.15				0.0013				0.0013
	318.15				0.0007				0.0006
	328.15				0.0014				0.0014

as the local composition effect from the chained segments in a polymer.

The NRTL residual term has the following form:

$$\frac{1}{r_1}\ln \gamma_1^{\mathrm{NRTL}} = z_2^{\,2}\left(\frac{\tau_{21}\exp(-\alpha\tau_{21})^2}{(z_1 + z_2\exp(-\alpha\tau_{21}))^2} + \frac{\tau_{12}\exp(-\alpha\tau_{12})}{(z_2 + z_1\exp(-\alpha\tau_{12}))^2}\right) \quad (9)$$

where τ_{12} and τ_{21} are NRTL parameters; α is the nonrandomness factor for which the value 0.25 was used. In this work, following Wu et al.[25] for temperature dependency of parameters τ_{12} and τ_{21}, the following relations were used:

$$\tau_{12} = a_w^{(1)}\left(\frac{T_0}{T}\right) + a_w^{(2)}\left(\frac{T_0}{T}\right)^2 \quad (10)$$

$$\tau_{21} = a_s^{(1)}\left(\frac{T_0}{T}\right) + a_s^{(2)}\left(\frac{T_0}{T}\right)^2 \quad (11)$$

where T_0 = 298.15 K, and $a^{(1)}$ and $a^{(2)}$ are the adjustable parameters. If the temperature range is not large, then we have $a_w^{(2)} = a_s^{(2)}$, as stated by Wu et al.[25]

The Wilson residual term has the following form:

$$-\frac{1}{Cr_1}\ln \gamma_1^{\mathrm{Wilson}} = \ln\left(z_1 + z_2\exp\left(-\frac{E_{21}}{CRT}\right)\right) + z_1\left(\frac{1 - \left(z_1 + z_2\exp\left(-\frac{E_{21}}{CRT}\right)\right)}{z_1 + z_2\exp\left(-\frac{E_{21}}{CRT}\right)}\right) + z_2\left(\frac{\exp\left(-\frac{E_{12}}{CRT}\right) - \left(z_2 + z_1\exp\left(-\frac{E_{12}}{CRT}\right)\right)}{z_2 + z_1\exp\left(-\frac{E_{12}}{CRT}\right)}\right) \quad (12)$$

where E_{12} and E_{21} are Wilson parameters. C is a parameter that represents the effective coordination number in the system for which the value 10 is used in this work. Equations 10 and 11 were also assumed for the temperature dependency of the Wilson parameters.

The results of fitting to the NRTL and Wilson models are shown in Table 6. From the obtained standard deviations reported in Table 6, we conclude that both of these models represent satisfactorily the solvent activity data for the investigated systems at different temperatures. As an example, the difference between the experimental and calculated solvents activities with the NRTL and Wilson models are shown at 298.15 K in Figures 7 and 8 for solutions of PPG400 in ethanol and 2-propanol, respectively. We also tested reliability of the other local composition models, NRF-NRTL[16] and NRF-Wilson[26] for the correlation of our experimental ethanol and 2-propanol activity data for the systems ethanol + PPG400 and 2-propanol + PPG400 at different temperatures. While both of these models have a good ability for correlation of 2-propanol activity data for the 2-propanol + PPG400 system, rather poor results are obtained for the ethanol activity data by these models. So that, standard deviation of the fit with the NRF-NRTL and NRF-Wilson models for the system 2-propanol + PPG400 are respectively 0.0044 and 0.0049 and for the system ethanol + PPG400 are respectively 0.0467 and 0.0467.

Conclusions

Accurate solvent activity data were determined for PPG400 + ethanol and PPG400 + 2-propanol systems at T = (298.15 to 328.15) K. These data were fitted to the Flory−Huggins model. It was found that both the solvent activity and Flory parameter decrease as the temperature is increased, indicating an increase of interaction between polymer and solvents by increasing the temperature. The activities of these alcohols tend to increase in the order ethanol > 2-propanol at working temperatures considered in this work. The results have also been correlated to the two local composition models, NRTL and Wilson. Good agreement with the experimental results was found with all of these models.

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