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Water Activities in Binary and Ternary Aqueous Systems of Poly(ethylene glycol) Dimethyl Ether 2000 and Poly(propylene glycol) 400 at T = (298.15, 308.15, and 318.15) K

Mohammed Taghi Zafarani-Moattar* and Nastaran Tohidifar

Physical Chemistry Department, University of Tabriz, Tabriz, Iran

ABSTRACT: Isopiestic measurements were used to obtain activities for aqueous solutions of poly(ethylene glycol) dimethyl ether 2000 + poly(propylene glycol) 400 and their corresponding binary aqueous solutions at temperatures T = (298.15, 308.15, and 318.15) K. The data obtained were used to calculate the vapor pressure of solution as a function of concentration. The effect of temperature on the vapor−liquid equilibrium (VLE) of binary and ternary systems has been studied. Furthermore, the activity results for binary and ternary aqueous solutions were correlated to the Flory−Huggins and Wilson models.

INTRODUCTION

Understanding the thermodynamics of the polymer solutions is important in practical applications such as polymerization, devolatilization, and the incorporation of plasticizers and other additives.[1−4] The thermodynamic characteristics of macromolecular solutions are closely related to the magnitude of relevant (segment−solvent and segment−segment) interaction energies. The thermodynamic quality of solvent is, therefore, a key factor that substantially affects the chain dimensions in solution and, also, how a dissolved polymer acts in an application. The classical mean-field theory derived by Flory and Huggins[5] is still widely used to represent the thermodynamic features of polymer solutions. The quality of solvent is characterized through the interaction parameter (χ). For a binary solution, χ_{12} measures the solvent (1)−segment (2) interaction and theoretically ranges from below zero for a very good solvent to 0.5 or greater.

A ternary solution that consists of two chemically different polymers and solvent can also be described by the extensions of the Flory−Huggins equations. Besides the solvent−segment interaction parameters (χ_{12}, χ_{13}), information on the thermodynamic interaction between the two macromolecular species (χ_{23}) should also be obtained for solvent (1) + polymer (2) + polymer (3) systems. All of these interaction parameters can be obtained using the Flory−Huggins equations. For obtaining these interaction parameters, one common method is to study vapor−liquid equilibrium (VLE) behavior of polymer solutions. Although for binary polymer solutions many VLE data are available, for the ternary polymer solutions the corresponding data are scarce.[6−12]

As far as we know, the VLE data for ternary aqueous solution of poly(ethylene glycol) dimethyl ether 2000 (PEGDME2000) + poly(propylene glycol) 400 (PPG400) have not been reported in literature. Recently some VLE data for binary solutions of PEGDME2000 + H_2O[13] and PPG400 + H_2O[13−16] have been reported. This work is the continuation of our study[17,18] on the thermodynamics of polymer + solvent systems. In the present report, experimental data on the VLE of binary aqueous solutions of PEGDME2000 and PPG400 and ternary water (1) + PEGDME2000 (2) + PPG400 (3) solutions are investigated through the isopiestic method at T = (298.15, 308.15, and 318.15) K. The data obtained were used to calculate vapor pressure of solutions as a function of concentration. The effect of temperature on the VLE of binary and ternary systems has been studied. Furthermore, the activity results for binary and ternary aqueous solutions were correlated to the Flory−Huggins[5] model and the Wilson model presented by Xu et al.[19]

EXPERIMENTAL SECTION

Materials. PEGDEME2000 (CAS No. 24991-55-7) and PPG400 (CAS No. 25322-69-4) were obtained from Merck and Fluka, respectively. Previously, the average molar masses of the PEGDME2000 and PPG400 were determined to be (2305[20] and 401[21]) g·mol^{-1}, respectively. The polymers were used as supplied by the manufacturers. Sodium chloride (NaCl, CAS No. 7647-14-5) with a minimum mass fraction purity 0.995 was obtained from Merck and was dried in an electrical oven at about 110 °C for 24 h prior to use. Double-distilled and deionized water was used.

Vapor−Liquid Equilibrium Measurements. In this study, the isopiestic method is used to obtain the activity of water in aqueous (PEGDME2000 + PPG400) solutions. It is based on the phenomenon that different solutions, when connected through the vapor space, approach equilibrium by transferring solvent mass by distillation. Equilibrium has been established once temperature and pressure are uniform throughout the system, provided that no concentration gradients exist in the liquid phase. At equilibrium, the chemical potentials of the solvent in each of the solutions in the closed system are identical. The equality of the solvent chemical potential implies the equality of the solvent activity. Since the solvent activity is known for one or more standard solutions, it will be known for each solution within the isopiestic system. The isopiestic apparatus used in this work was similar to the one used by Ochs et al.[22] This apparatus consisted of a seven-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions;

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Table 1. Isopiestic Equilibrium Weight Fractions, Osmotic Coefficients, Water Activities, and Vapor Pressures of Water (1) + PEGDME2000 (2) and Water (1) + PPG400 (3) at T = (298.15, 308.15, and 318.15) K

w_3	w_{ref}[a]	ϕ	a_1	p/kPa	w_2	w_{ref}	ϕ	a_1	p/kPa
Water (1) + PPG400 (3)					Water (1) + PEGDME2000 (2)				
T/K = 298.15									
0.1478	0.0133	0.924	0.9924	3.149	0.1306	0.8006	0.931	0.9961	3.160
0.1664	0.0153	0.923	0.9912	3.145	0.1539	0.0098	0.926	0.9944	3.155
0.2427	0.024	0.923	0.9861	3.129	0.1978	0.0133	0.924	0.9924	3.149
0.3128	0.0325	0.926	0.9810	3.113	0.2065	0.0158	0.923	0.9909	3.144
0.3660	0.0384	0.929	0.9774	3.101	0.2183	0.0153	0.923	0.9912	3.145
0.4209	0.0482	0.936	0.9712	3.082	0.2476	0.0206	0.923	0.9881	3.135
0.5983	0.0636	0.948	0.9611	3.049	0.2653	0.0240	0.923	0.9861	3.129
0.6134	0.0642	0.949	0.9606	3.048	0.2710	0.0237	0.923	0.9863	3.129
0.6640	0.0699	0.954	0.9568	3.036	0.3032	0.0325	0.926	0.9810	3.113
0.7882	0.1501	0.992	0.9306	2.953	0.3172	0.0341	0.927	0.9800	3.110
0.8448	0.1454	1.048	0.8959	2.842	0.3320	0.0384	0.929	0.9774	3.101
					0.3582	0.0482	0.936	0.9712	3.082
					0.4070	0.0638	0.948	0.9609	3.049
					0.4096	0.0642	0.949	0.9606	3.048
					0.4250	0.0699	0.954	0.9568	3.036
					0.4789	0.0951	0.980	0.9385	2.977
					0.4921	0.1501	0.992	0.9306	2.953
					0.5353	0.1254	1.019	0.9139	2.899
					0.5459	0.1324	1.029	0.9077	2.880
					0.5679	0.1454	1.048	0.8959	2.842
					0.6341	0.1804	1.107	0.8605	2.730
					0.6357	0.1825	1.110	0.8583	2.723
T/K = 308.15									
0.1443	0.0124	0.922	0.9929	5.535	0.1679	0.0081	0.927	0.9954	5.549
0.2100	0.0166	0.920	0.9905	5.522	0.1982	0.0124	0.922	0.9929	5.535
0.2735	0.0232	0.920	0.9866	5.500	0.2011	0.0117	0.923	0.9933	5.538
0.4240	0.0320	0.923	0.9813	5.471	0.2281	0.0166	0.920	0.9905	5.522
0.4701	0.0345	0.924	0.9798	5.462	0.2506	0.0175	0.920	0.9899	5.519
0.5970	0.0465	0.931	0.9724	5.421	0.3122	0.0286	0.922	0.9834	5.482
0.7500	0.0634	0.945	0.9613	5.359	0.3428	0.0345	0.924	0.9798	5.462
0.7695	0.0716	0.952	0.9557	5.328	0.3688	0.0435	0.929	0.9743	5.431
0.8065	0.0920	0.973	0.9410	5.245	0.4291	0.0642	0.954	0.9608	5.356
0.8064	0.0985	0.981	0.9361	5.218	0.4296	0.0634	0.945	0.9613	5.359
0.8599	0.1385	1.034	0.9025	5.031	0.4518	0.0716	0.952	0.9557	5.328
0.8723	0.1619	1.071	0.8802	4.906	0.4818	0.0868	0.968	0.9448	5.267
					0.5689	0.1297	1.022	0.9104	5.074
					0.7011	0.1999	1.139	0.8391	4.676
T/K = 318.15									
0.0892	0.0096	0.923	0.9945	9.455	0.1704	0.0076	0.926	0.9956	9.466
0.1253	0.0102	0.922	0.9941	9.452	0.1840	0.0106	0.922	0.9939	9.450
0.1898	0.0133	0.919	0.9924	9.435	0.1907	0.0115	0.921	0.9934	9.445
0.2597	0.0173	0.918	0.9901	9.414	0.2384	0.0159	0.918	0.9909	9.421
0.4170	0.0219	0.918	0.9874	9.388	0.3126	0.0260	0.918	0.9850	9.365
0.5134	0.0251	0.918	0.9855	9.370	0.3840	0.0407	0.925	0.9761	9.280
0.5439	0.0257	0.918	0.9852	9.367	0.3953	0.0458	0.928	0.9799	9.250
0.5784	0.0285	0.919	0.9835	9.351	0.4320	0.0617	0.940	0.9626	9.151
0.6004	0.0315	0.920	0.9817	9.334	0.4432	0.0640	0.942	0.9611	9.137
0.6696	0.0382	0.923	0.9777	9.295	0.5196	0.0891	0.966	0.9434	8.968
0.6944	0.0411	0.925	0.9759	9.278	0.5332	0.0966	0.975	0.9378	8.915
0.7375	0.0519	0.932	0.9690	9.213	0.6110	0.1330	1.022	0.9078	8.629
0.7696	0.0640	0.942	0.9611	9.137	0.6208	0.1389	1.031	0.9026	8.579
0.8142	0.0891	0.966	0.9434	8.968	0.7201	0.1910	1.118	0.8499	8.077
0.8271	0.0966	0.975	0.9378	8.915					
0.8597	0.1330	1.022	0.9078	8.629					
0.8733	0.1389	1.031	0.9026	8.579					

[a] w_{ref} represents the mass fraction of the isopiestic reference (NaCl solutions).

one flask contained the pure PEGDME2000, and one flask contained the pure PPG400. Two flasks contained (PEGDME2000 + PPG400) solutions, and the central flask was used as a water reservoir. For binary systems, this apparatus consisted of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions; two flasks contained the pure PEGDME2000 or PPG400, and the central flask was used as a water reservoir. The apparatus was held in a constant-temperature bath for at least 120 h for equilibrium. During the equilibration process, the manifold was removed at least once a day, and the samples were agitated. After the third day, the samples were not agitated but left in the bath to approach their final equilibrium conditions. The temperature was controlled to within 0.01 K by a (Julabo, MD, Germany) temperature controller. After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance (Shimadzu, 321-34553, Shimadzu Co., Japan) with a precision of $\pm 1 \cdot 10^{-4}$ g. From the mass of each flask after equilibrium and the initial mass of PEGDME2000 and PPG400, the mass fraction of each solution was calculated. The water activity for the standard aqueous NaCl solutions at different concentrations had been calculated from the correlation of Colin et al.[23] It was assumed that the equilibrium was reached when the differences between the mass fractions of two standard solutions were less than 1 %. In all cases, averages of the mass fractions of two standard solutions are reported. The accuracy of the method depends upon the standard solutions, sample mixing during the equilibrium period, temperature stability, and the time allowed for the equilibrium process. The uncertainty in the measurement of solvent activity was estimated to be $\pm 2 \cdot 10^{-4}$.

RESULTS AND DISCUSSION

In this work, the isopiestic measurements at T = (298.15, 308.15, and 318.15) K were carried out for water (1) + PEGDME 2000 (2) + PPG 400 (3) solutions and their corresponding binary solutions to study the VLE behavior of these systems. For the understanding of interactions in liquids, the activity or osmotic coefficients of the different components are of great interest. At isopiestic equilibrium, the activity of the solvent in the reference and sample solutions must be the same. Therefore, the isopiestic equilibrium mass fractions with reference standard solutions of NaCl in water, as reported in Table 1, enabled the calculation of the solvent activity, a_1, in the solutions of water (1) + PEGDME2000 (2) and water (1) + PPG400 (3) from that of reference solutions using the relations

$$\ln a_1 = -\nu m_{\text{NaCl}} \phi_{\text{NaCl}} M_1 \quad (1)$$

$$m_{\text{NaCl}} = \frac{w_{\text{NaCl}}}{M_{\text{NaCl}}(1 - w_{\text{NaCl}})} \quad (2)$$

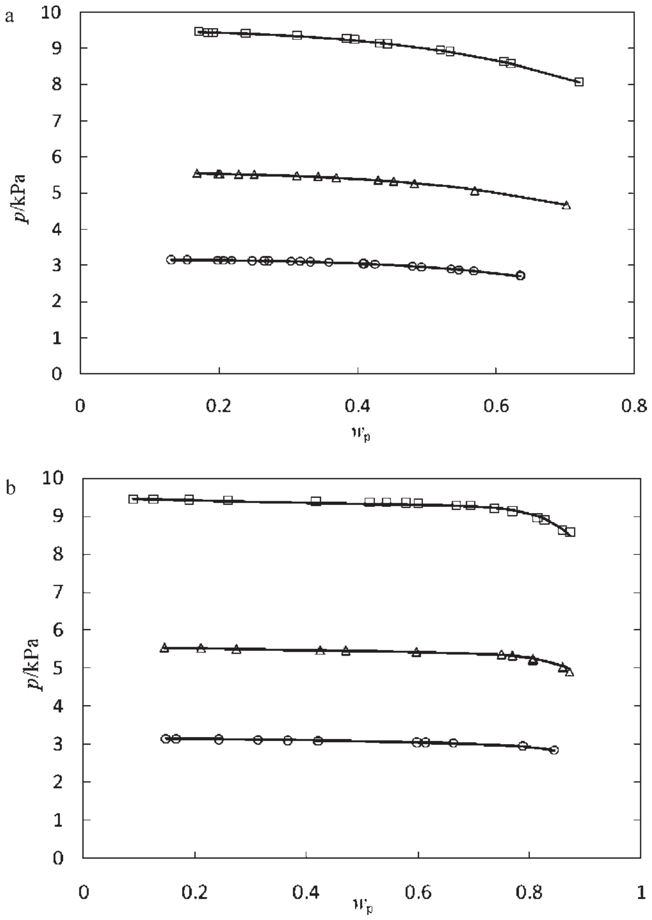

Figure 1. Plot of vapor pressure of water vapor of the binary systems against the mass fraction of polymer, w_p: (a) water (1) + PEGDME2000 (2) system, (b) water (1) + PPG400 (3) system; ○, 298.15 K; △, 308.15 K; □, 318.15 K; —, modified Wilson model (eq 8).

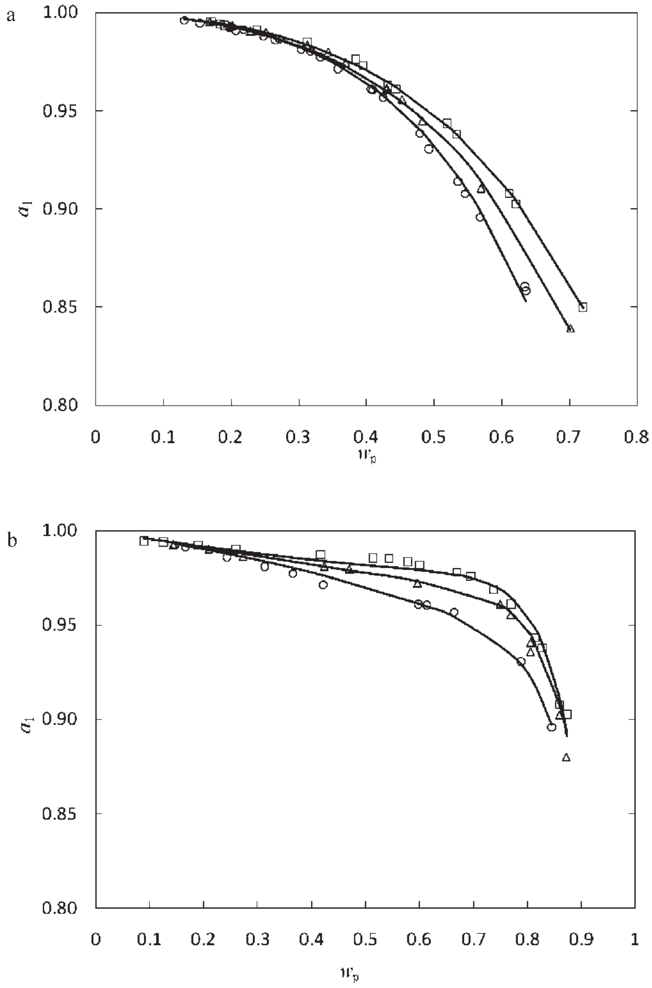

Figure 2. Plot of water activity of the binary systems against the mass fraction of polymer, w_p: (a) water (1) + PEGDME2000 (2) system, (b) water (1) + PPG400 (3) system; ○, 298.15 K; △, 308.15 K; □, 318.15 K; —, modified Wilson model (eq 8).

where ν is the sum of stoichiometric numbers of anion and the cation in the reference solutions, m_{NaCl} and w_{NaCl} are respectively the substance concentration and mass fraction of NaCl which is in isopiestic equilibrium with the polymer solutions, M_1 and M_{NaCl} are respectively the molar masses of the solvent and NaCl; and ϕ_{NaCl} is the osmotic coefficient of the isopiestic reference standard, calculated at m_{NaCl}. The necessary ϕ_{NaCl} values at any m_{NaCl} were calculated from the correlation given by Colin et al.[23] From the calculated solvent activity data, the vapor pressures of water 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 water, respectively. The second virial coefficient of water vapor was calculated using the equation provided by Rard and Platford.[24] The molar volume of liquid water was calculated using the density of water at different temperatures.[25] The vapor pressure of pure water was calculated using the equation of state of Saul and Wagner.[26] After the establishment of isopiestic equilibrium, water activities were calculated using eq 1. The values of p for studied systems were calculated using eq 3. The results are collected in Table 1.

In Figure 1 parts a and b, the experimental vapor pressure values for binary water (1) + PEGDME2000 (2) and water (1) + PPG400 (3) solutions are plotted against the mass fraction of polymer at T = (298.15, 308.15, and 318.15) K, respectively. As can be seen from Figure 1a,b, the vapor pressure for the investigated polymer solutions increases by increasing temperature. This is because the polymers become more hydrophobic with increasing temperature. Experimental water activity data for binary solutions at different temperatures are shown in Figure 2a,b. Sadeghi and Shahebrahimi[13] have reported experimental water activity data for water (1) + PEGDME2000 (2) at 298.15 K in the mass fraction range of 0.1753 to 0.6422 by an isopiestic method and 0.0112 to 0.2674 by a vapor pressure osmometry (VPO) method; also, they presented water activity data for this system at (303.15 and 308.15) K in the dilute region.[13] In Figure 3a,b, comparisons of the experimental water activity data measured in this work with those taken from the literature have been made for water (1) + PEGDME2000 (2) and water (1) + PPG400 (3) systems at T = 298.15 K, respectively. As can be seen in Figure 3a,b, there is

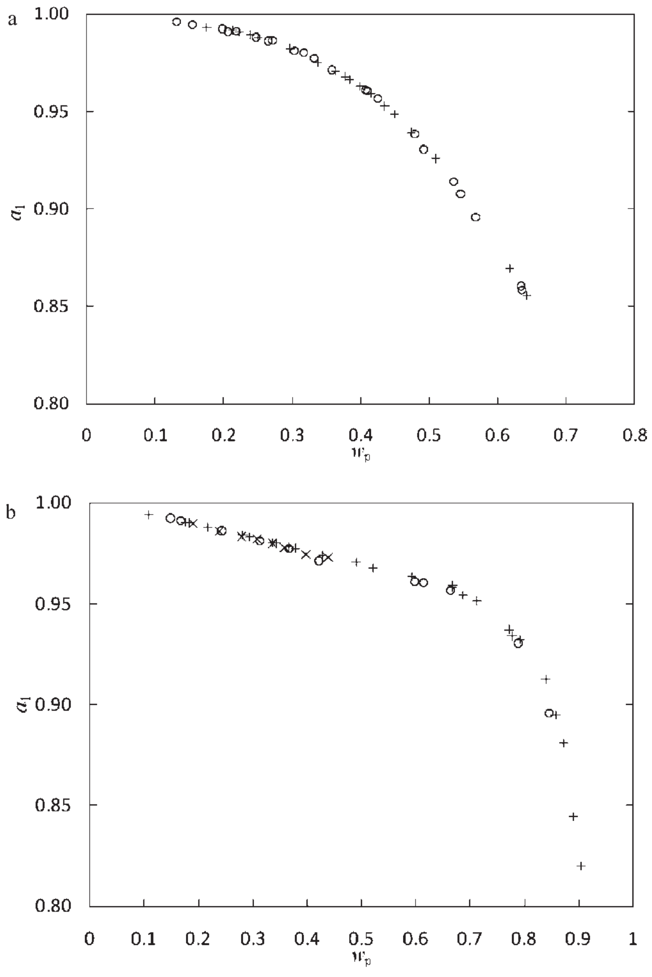

Figure 3. Plot of water activity of the binary systems against the mass fraction of polymer, w_p, at $T = 298.15$ K: (a) water (1) + PEGDME2000 (2) system; ○, this work; +, ref 14; (b) water (1) + PPG400 (3) system, ○, this work; +, ref 14; ×, ref 16.

good agreement between the results obtained in this work and those taken from the literature.

As can be seen from Figure 2a, the plot for PEGDME shows a markedly larger negative slope of the water activity or vapor pressure against polymer mass fraction above mass fractions of about 0.4 at $T = (298.15, 308.15, \text{and } 318.15)$ K, which implies that there is strong interaction between the water and the segment of PEGDME at higher mass fractions of polymer. The same behavior is also observed for aqueous PPG solutions with polymer mass fractions greater than about 0.8. At $T = (298.15, 303.15, \text{and } 308.15)$ K, Sadeghi and Shahebrahimi[13] have also observed similar behavior for these polymer solutions at high mass fractions of polymers.

Table 2 reports the water activities and vapor pressures of the ternary water (1) + PEGDME2000 (2) + PPG400 (3) system at $T = (298.15, 308.15, \text{and } 318.15)$ K. The lines of constant water activity or vapor pressure of the studied system at corresponding temperatures are plotted in Figures 4, 5, and 6. As can be seen in Table 2, in fact four points on each line in Figures 4, 5, and 6 have a constant water activity or chemical potential, and thus these points are in equilibrium.

Correlation of Data. Water activity values a_1 at each temperature reported in Table 1 were fitted to the original

Table 2. Water Activity and Vapor Pressure for the Water (1) + PEGDME2000 (2) + PPG400 (3) System for Different Mass Fractions, w, at $T = (298.15, 308.15, \text{and } 318.15)$ K

w_2	w_3	w_{ref}	a_1	p/kPa
		Water (1) + PEGDME2000 (2) + PPG400 (3)		
		T/K = 298.15		
0.1978	0.0000	0.0133	0.9924	3.149
0.1164	0.0642			
0.0586	0.1056			
0.0000	0.1478			
0.2183	0.0000	0.0153	0.9912	3.145
0.1311	0.0642			
0.0499	0.1315			
0.0000	0.1664			
0.2653	0.0000	0.0240	0.9861	3.129
0.1335	0.1199			
0.0610	0.1874			
0.0000	0.2427			
0.3032	0.0000	0.0325	0.9810	3.113
0.1693	0.1340			
0.0761	0.2310			
0.0000	0.3128			
0.3320	0.0000	0.0384	0.9774	3.101
0.2032	0.1248			
0.0782	0.2658			
0.0000	0.3660			
0.3582	0.0000	0.0482	0.9712	3.082
0.2426	0.1213			
0.1037	0.2761			
0.0000	0.4209			
0.3984	0.0000	0.0636	0.9611	3.049
0.2414	0.1835			
0.1234	0.3532			
0.0000	0.5983			
0.4096	0.0000	0.0642	0.9606	3.048
0.2486	0.1867			
0.1266	0.3620			
0.0000	0.6134			
0.4250	0.0000	0.0699	0.9568	3.036
0.2612	0.1852			
0.1325	0.3819			
0.0000	0.6640			
0.4921	0.0000	0.1501	0.9306	2.953
0.3233	0.2251			
0.1701	0.4866			
0.0000	0.7882			
0.5679	0.0000	0.1454	0.8959	2.842
0.3814	0.2582			
0.1854	0.5553			
0.0000	0.8448			
		T/K = 308.15		
0.1982	0.0000	0.0124	0.9929	5.535
0.1012	0.0734			
0.0417	0.1200			
0.0000	0.1443			

Table 2. Continued

w_2	w_3	w_{ref}	a_1	p/kPa
0.2281	0.0000	0.0166	0.9905	5.522
0.1195	0.1039			
0.0531	0.1617			
0.0000	0.2100			
0.2676	0.0000	0.0232	0.9866	5.500
0.1622	0.1022			
0.0710	0.2011			
0.0000	0.2735			
0.3149	0.0000	0.0320	0.9813	5.471
0.2024	0.1201			
0.0968	0.2612			
0.0000	0.4240			
0.3428	0.0000	0.0345	0.9798	5.462
0.2100	0.1394			
0.1095	0.2723			
0.0000	0.4701			
0.3539	0.0000	0.0465	0.9724	5.421
0.2322	0.1466			
0.1179	0.3333			
0.0000	0.5970			
0.4296	0.0000	0.0634	0.9613	5.359
0.2845	0.1902			
0.1502	0.4357			
0.0000	0.7500			
0.4518	0.0000	0.0716	0.9557	5.328
0.2967	0.2033			
0.1553	0.4582			
0.0000	0.7695			
0.4973	0.0000	0.0920	0.9410	5.245
0.3362	0.2236			
0.1690	0.4920			
0.0000	0.8009			
0.5072	0.0000	0.0985	0.9361	5.218
0.3432	0.2266			
0.1726	0.5005			
0.0000	0.8064			
0.5882	0.0000	0.1385	0.9025	5.031
0.4042	0.2613			
0.1912	0.5661			
0.0000	0.8599			
0.6166	0.0000	0.1619	0.8802	4.906
0.4139	0.2892			
0.2055	0.5947			
0.0000	0.8723			
		T/K = 318.15		
0.1460	0.0000	0.0096	0.9945	9.455
0.0885	0.0547			
0.0508	0.0763			
0.0000	0.1253			
0.2079	0.0000	0.0102	0.9941	9.452
0.1253	0.0602			
0.0529	0.1270			
0.0000	0.1819			

Table 2. Continued

w_2	w_3	w_{ref}	a_1	p/kPa
0.2156	0.0000	0.0133	0.9924	9.435
0.1391	0.0639			
0.0571	0.1329			
0.0000	0.1898			
0.2282	0.0000	0.0173	0.9901	9.414
0.1337	0.0802			
0.0581	0.1606			
0.0000	0.2597			
0.2420	0.0000	0.0219	0.9874	9.388
0.1661	0.1047			
0.0759	0.2185			
0.0000	0.4170			
0.2932	0.0000	0.0251	0.9855	9.370
0.1759	0.1229			
0.0889	0.2662			
0.0000	0.5134			
0.3132	0.0000	0.0257	0.9852	9.367
0.1857	0.1346			
0.0937	0.2836			
0.0000	0.5439			
0.3180	0.0000	0.0285	0.9835	9.351
0.1860	0.1550			
0.0948	0.2993			
0.0000	0.5784			
0.3248	0.0000	0.0315	0.9817	9.334
0.1997	0.1447			
0.1054	0.3190			
0.0000	0.6004			
0.3286	0.0000	0.0351	0.9796	9.313
0.2290	0.1267			
0.1077	0.3404			
0.0000	0.6242			
0.3549	0.0000	0.0382	0.9777	9.295
0.2220	0.1609			
0.1154	0.3495			
0.0000	0.6458			
0.3684	0.0000	0.0454	0.9732	9.252
0.2306	0.1890			
0.1377	0.3730			
0.0000	0.6587			
0.4432	0.0000	0.0640	0.9611	9.137
0.2881	0.2088			
0.1559	0.4454			
0.0000	0.7458			
0.4515	0.0000	0.0717	0.9558	9.087
0.2934	0.2157			
0.1556	0.4712			
0.0000	0.7553			
0.5196	0.0000	0.0891	0.9434	8.968
0.3358	0.2433			
0.1764	0.5039			
0.0000	0.8142			
0.5332	0.0000	0.0966	0.9378	8.915
0.3452	0.2433			
0.1813	0.5190			
0.0000	0.8271			

Table 2. Continued

w_2	w_3	w_{ref}	a_1	p/kPa
0.6110	0.0000	0.1330	0.9078	8.629
0.4006	0.2784			
0.1975	0.5707			
0.0000	0.8597			
0.6208	0.0000	0.1389	0.9026	8.579
0.4050	0.2935			
0.2033	0.5808			
0.0000	0.8733			

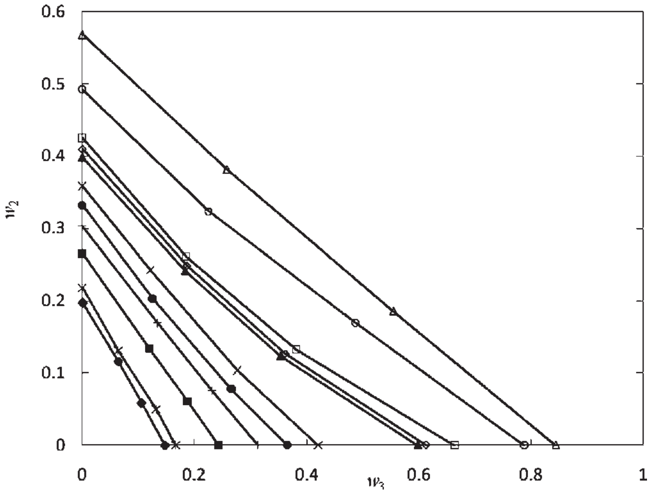

Figure 4. Constant water activity curves for the water (1) + PEGDME2000 (2) + PPG400 (3) system at 298.15 K: ♦, 0.9924; ∗, 0.9912; ■, 0.9861; +, 0.9810; ●, 0.9774; ×, 0.9712; ▲, 0.9611; ◊, 0.9606; □, 0.9568; ○, 0.9306; △, 0.8959.

Flory−Huggins model[5] which has the following form

$$\ln a_1 = \ln \varphi_1 + \left(1 - \frac{1}{r_2}\right)(1 - \varphi_1) + \chi_{12}(1 - \varphi_1)^2 \tag{4}$$

In eq 4, φ_1 is the volume fraction of solvent, χ_{12} is the Flory parameter, and r_2 is the ratio of the molar volume of polymer and solvent. The result of fitting to eq 4 is given in Table 3. The average relative deviation (ARD%) values for a_1 given in Table 3 and Figure 2 indicate that eq 4 represents the experimental water activity data for water (1) + PEGDME2000 (2) system satisfactorily from dilute to high polymer concentrations. However, although for most of polymer solutions the Flory−Huggins model gives good results, the model cannot satisfactorily correlate the experimental water activity data for the water (1) + PPG400 (3) system, especially at high polymer concentrations. For this system we found that for polymer mass fractions less than 0.4 the quality of fitting is satisfactory, as can be seen from lower ARD% values reported in Table 3. The χ_{12} value reported in Table 3 for the water (1) + PEGDME2000 (2) system increases by increasing temperature. The same behavior is also observed for aqueous PPG solutions with polymer mass fractions less than 0.5. This increase in χ_{12} indicates that as the temperature increases the interaction between polymer and water become weaker. However, since there is a little difference between the obtained χ_{12} values, the temperature has only small effect on the interaction between polymer and water.

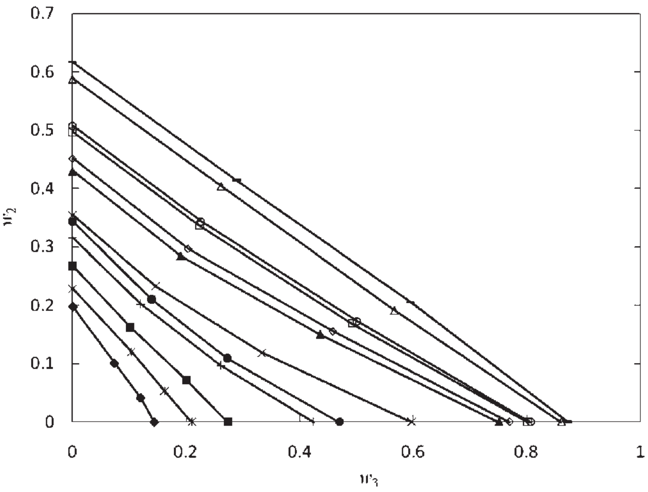

Figure 5. Constant water activity curves for the water (1) + PEGDME2000 (2) + PPG400 (3) system at 308.15 K: ♦, 0.9929; ∗, 0.9905; ■, 0.9866; +, 0.9813; ●, 0.9798; ×, 0.9724; ▲, 0.9613; ◊, 0.9557; □, 0.9410; ○, 0.9361; △, 0.9025; −, 0.8802.

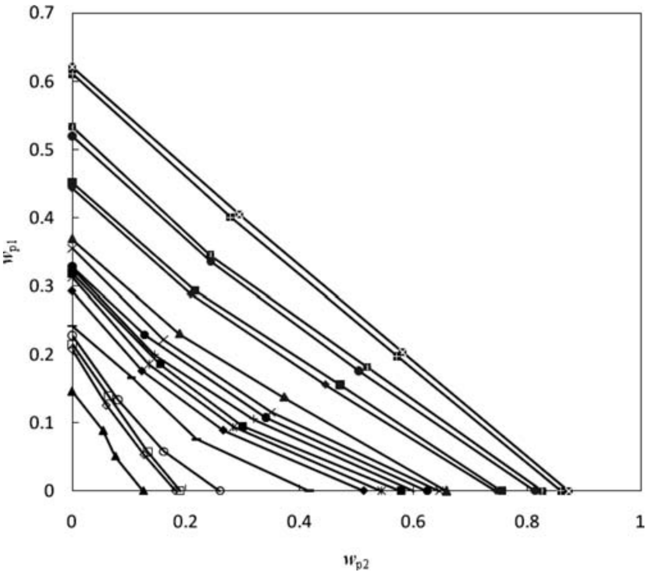

Figure 6. Constant water activity curves for the water (1) + PEGDME2000 (2) + PPG400 (3) system at 318.15 K: ▲, 0.9945; ◊, 0.9941; □, 0.9924; ○, 0.9901; −, 0.9874; ♦, 0.9855; ∗, 0.9852; ■, 0.9835; +, 0.9817; ●, 0.9796; ×, 0.9777; gray ▲, 0.9732; gray ♦, 0.9611; gray ■, 0.9558; gray ●, 0.9434; white *, 0.9378; white +, 0.9078; white ×, 0.9026.

For a three-component mixture, where component 1 is the solvent and components 2 and 3 are polymers, eq 4 can be presented as[5]

$$\ln a_1 = \left[\ln \phi_1 + (1 - \phi_1) - \phi_2\left(\frac{1}{r_2}\right) - \phi_3\left(\frac{1}{r_3}\right) + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(\phi_2 + \phi_3) - \chi_{23}\left(\frac{1}{r_2}\right)\phi_2\phi_3\right] \tag{5}$$

where ϕ_2, ϕ_3, r_2, r_3, χ_{13}, and χ_{23} represent respectively the volume fraction of polymer (2), volume fraction of polymer (3), the ratio of the molar volume of polymer (2) and solvent, the ratio of the molar volume of polymer (3) and solvent, the Flory interaction

Table 3. Parameter of the Flory−Huggins Model (eq 4) for the Studied Binary Systems

T/K	polymer mass fraction range	χ_{ij}[a]	ARD%
	Water (1) + PEGDME2000 (2)		
298.15	0.1306−0.6357	0.4291	0.36
308.15	0.1679−0.7011	0.5208	0.90
318.15	0.1704−0.7201	0.5847	1.23
	Water (1) + PPG400 (3)		
298.15	0.1478−0.8448	1.1072	6.55
	0.1478−0.4209	0.6228	0.31
308.15	0.1443−0.8723	1.2581	7.17
	0.1443−0.4240	0.6872	0.47
318.15	0.0892−0.8733	1.2297	8.04
	0.0892−0.4170	0.7197	0.40

[a] i represents water; j represents polymer 2 or 3.

parameter between solvent (1) and polymer (3), and the Flory interaction parameter between polymer (2) and polymer (3). However, on the basis of eq 5, the χ_{23} parameter is dependent on the χ_{12} and χ_{13} values, and on the other hand these interaction parameters are concentration-dependent; therefore, the χ_{23} values calculated from eq 5 should be considered as estimated values.

The χ_{12} and χ_{13} parameters determined in binary polymer solutions have been used in calculations for the χ_{23} parameter in the ternary solution. Since the Flory−Huggins model can only correlate the experimental water activity data for the water (1) + PPG400 (3) system with acceptable accuracy for polymer mass fractions less than 0.4, therefore in calculation of χ_{23} by the eq 5, we used χ_{13} = 0.6228, 0.6872, and 0.7197 from Table 3 for the water (1) + PPG400 (3) system, and in fitting water activity data for ternary solutions reported in Table 2 we only considered those data in which the PPG mass fractions do not exceed 0.4. The obtained negative χ_{23} values at each temperature presented in Table 4 may indicate that there are strong interactions between the two polymers.

As pointed out by Csáki et al.[8] some of the shortcomings owing to the approximation used in the calculations for χ_{23} can be eliminated by determining the $\chi_{1,23}$ interaction parameter for two polymer−component mixtures on the theoretical basis suggested by Panayiotou and Vera.[9] In principle, the $\chi_{1,23}$ parameter does not provide information directly on the segmental interactions between chemically different polymers, but this parameter may be related to χ_{23}. In fact, as pointed out by Panayiotou and Vera,[9] the term $\chi_{1,23}$ considerably simplifies the presentation of data for ternary systems with a general formalism for the treatment of polymer solutions. For the calculation of this mixed $\chi_{1,23}$ parameter, knowledge of χ_{12} and χ_{13} is not necessary.

The $\chi_{1,23}$ parameter can be calculated from the water activity data as follows[9]

$$\ln a_1 = \left[\ln \phi_1 + \left(1 - \frac{r_1}{r_{23}}\right)\phi_{23} + \chi_{1,23}\phi_{23}^2\right] \qquad (6)$$

This relation is similar to the Flory−Huggins model (eq 4) for a binary solution. From the fitting of water activity data for ternary solutions (again the data corresponding to the PPG mass fractions greater than 0.4 were discarded) to eq 6, we obtained $\chi_{1,23}$ values which are also collected in Table 4. The $\chi_{1,23}$ values may be regarded as a mean parameter characterizing the solvent−segxment interactions in a solution of chemically different macromolecules.[8] From the comparison of χ_{12} and $\chi_{1,23}$ values reported respectively in Tables 3 and 4, it can be seen that at each temperature the $\chi_{1,23}$ value is larger than the corresponding χ_{12} value. This indicates that, due to the interaction between segments of PPG and PEGDME, the interaction between solvent and segment of PEGDME is reduced.

Table 4. Parameters of Flory−Huggins Model (eqs 6 and 7), $\chi_{1,23}$ and χ_{23}, for the Ternary System Water (1) + PEGDME2000 (2) + PPG400 (3)

T/K	$\chi_{1,23}$	ARD%	χ_{23}	ARD%[a]
298.15	0.6068	0.95	−6.8939 (−6.4534)[b]	0.90
308.15	0.6823	1.31	−7.8441 (−6.6722)[b]	1.40
318.15	0.7064	1.14	−4.9767 (−4.2301)[b]	1.19

[a] The necessary Flory−Huggins parameters for binary polymer solutions were taken from Table 3. [b] The values were obtained using $\chi_{1,23}$ values and eq 7.

Panayiotou and Vera[9] obtained the following relation between $\chi_{1,23}$ and individual solvent−segment and segment−segment interaction parameters

$$\chi_{1,23} = [(\chi_{12}\phi_2 + \chi_{13}\phi_3)(1 - \phi_1) - \chi'_{23}\phi_2\phi_3]/\phi_{23}^2 \qquad (7a)$$

where

$$\phi_{23} = \sum_{i=2}^{n} \phi_i = 1 - \phi_1 \qquad (7b)$$

$$r_{23} = \sum_{i=2}^{n} x_i r_i \qquad (7c)$$

and

$$\chi'_{23} = \frac{r_1}{r_2}\chi_{23} \qquad (7d)$$

Alternatively, for obtaining χ_{23} values, first the $\chi_{1,23}$ values were calculated from the fitting of water activity data for ternary solutions with the help of eq 6, and then the χ_{23} values were determined using the eq 7. These χ_{23} values are also reported in Table 4. There is fairly good agreement between the χ_{23} values obtained with the two different methods.

From the survey of literature we found that there is also another model which has been developed recently by Xu et al.[19] for binary and multicomponent polymer solutions. Xu et al.[19] have explicitly introduced a new modified Wilson equation for the calculation of VLE of aqueous polymer solutions which has the following form:

$$\ln a_i = \ln X_i + \sum_{k=1}^{m} X_k\left(1 - \frac{q_i}{q_k}\right) + \frac{q_i}{\alpha}\ln\frac{X_i}{\Phi_i} + \frac{q_i}{\alpha}\sum_{k=1}^{m}\left(\frac{q_k r_i}{q_i r_k} - 1\right)\Phi_k + \frac{q_i}{\alpha}\left[-\ln\left(\sum_{k=1}^{m} X_k G_{ki}\right) + 1 - \sum_{k=1}^{m}\frac{X_k G_{ik}}{\sum_{j=1}^{m} X_j G_{jk}}\right] \qquad (8a)$$

Table 5. Parameters of Modified Wilson Model (eq 8) for the Studied Binary Systems at Each Temperature

T/K	polymer concentration range	Xu−Wilson model τ_{12}	τ_{21}	α	ARD%
Water (1) + PEGDME2000 (2)					
298.15	0.1306−0.6357	0.4787	−0.4787	0.3	0.21
308.15	0.1679−0.7011	−2.1055	3.8897	0.3	0.13
318.15	0.1704−0.7201	−2.0646	4.0486	0.3	0.11
Water (1) + PPG400 (3)					
298.15	0.1478−0.8448	−1.5417	3.5802	0.3	0.19
308.15	0.1443−0.8723	−1.4651	3.4761	0.3	0.07
318.15	0.0892−0.8733	−1.4046	3.3554	0.3	0.38

where

$$X_i = \frac{N_i q_i}{\sum_{k=1}^{m} N_k q_k} \tag{8b}$$

$$\Phi_i = \frac{N_i r_i}{\sum_{k=1}^{m} N_k r_k} \tag{8c}$$

$$q_i = r_i\left[1 - \alpha\left(1 - \frac{1}{r_i}\right)\right] \tag{8d}$$

$$G_{ki} = \exp(-\alpha\tau_{ki}) \tag{8e}$$

$$\tau_{ki} = \left(\frac{1}{\alpha}\right)\left(\frac{\varepsilon_{ki} - \varepsilon_{ii}}{RT}\right) \tag{8f}$$

r_i represents the number of the segment i, and α is the nonrandomness factor and is set to 0.3 for both binary and ternary systems. It is very easy to reduce this equation for binary aqueous polymer solutions. However, the reliability of this model has not tested for ternary polymer solutions. To see the performance of the modified Wilson model,[19] we also fitted our water activity data for binary and ternary polymer solutions with eq 8.

The results of fitting of experimental binary activity data taken from Table 1 to eq 8 are given in Table 5 at each temperature. From the reported low ARD% with eq 8, we conclude that the quality of fitting with the modified Wilson model (eq 8) is better than the original Flory−Huggins equation for both binary systems.

Figure 1a,b shows the comparison between experimental and calculated values of vapor pressure by modified Wilson model[19] for both binary polymer solutions at the temperatures of T = (298.15, 308.15, and 318.15) K. Also the comparison between experimental and calculated values of water activity by the modified Wilson model[19] for both binary polymer solutions at the temperatures T = (298.15, 308.15, and 318.15) K has been shown in Figure 2a,b. A slight temperature dependence on a_1 values is observed along the concentration range studied. The differences between the experimental and calculated water activities with the modified Wilson[19] model are shown at different temperatures in Figure 7a,b for water (1) + PEGDME2000 (2) and water (1) + PPG400 (3) systems, respectively.

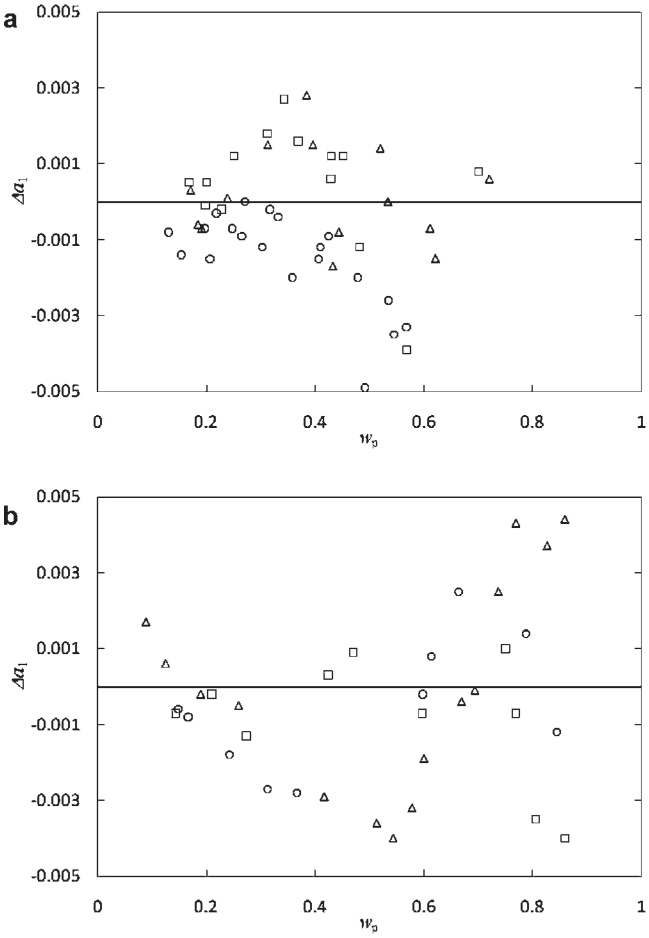

Figure 7. Deviations $\Delta a_1 = a_{(\text{expt})} - a_{(\text{calc})}$ of experimental water activity $a_{(\text{expt})}$ at different temperatures from values $a_{(\text{calc})}$ obtained using the modified Wilson model with temperature dependency (eqs 8 and 9) as a function of mass fraction of polymer, w_p: (a) water (1) + PEGDME2000 (2) system, (b) water (1) + PPG400 (3) system; ○, 298.15 K; △, 308.15 K; □, 318.15 K.

Table 6. Parameters of the Modified Wilson Model (eq 8) for the Ternary System Water (1) + PEGDME2000 (2) + PPG400 (3)

T/K	w_2	w_3	Xu−Wilson model τ_{23}	τ_{32}	α	ARD%[a]
298.15	0.0499−0.3814	0.0642−0.5553	−1.5406	2.1088	0.3	0.83
308.15	0.0417−0.4139	0.0616−0.5947	−0.8062	0.9941	0.3	0.22
318.15	0.0508−0.4050	0.0547−0.5808	−0.7577	0.9867	0.3	0.14

[a] The necessary modified Wilson parameters for binary polymer solutions were taken from Table 5.

In this work we have used the modified Wilson model[19] for correlating the experimental water activity data for ternary systems at each temperature. The results of fitting to eq 8 are given in Table 6. From the reported low ARD% with eq 8, we conclude that the quality of fitting with the modified Wilson model[19] for the ternary system (eq 8) with two parameters is

Table 7. Parameters of the Modified Wilson Model with Temperature Dependency (eqs 8 and 9) for Studied Binary Systems

		Xu–Wilson model				
T/K	polymer concentration range	b	c	d	α	ARD%
		Water (1) + PEGDME2000 (2)				
298.15–318.15		6.1127	−1.8232	−0.7951	0.3	0.14
298.15	0.1306–0.6357	0.15				0.15
308.15	0.1679–0.7011	0.16				0.16
318.15	0.1704–0.7201	0.12				0.12
		Water (1) + PPG400 (3)				
298.15–318.15		4.3996	−0.5849	−1.1283	0.3	0.24
298.15	0.1478–0.8448	0.19				0.19
308.15	0.1443–0.8723	0.20				0.20
318.15	0.0892–0.8733	0.30				0.30

Table 8. Parameters of the Modified Wilson Model with Temperature Dependency (eqs 8 and 9) for the Ternary System Water (1) + PEGDME2000 (2) + PPG400 (3)

T/K	w_2	w_3	b	c	d	α	ARD%
298.15–318.15			0.1061	−0.9849	1.7980	0.3	0.23
298.15	0.0499–0.3814	0.0642–0.5553					0.38
308.15	0.0417–0.4139	0.0616–0.5947					0.22
318.15	0.0508–0.4050	0.0547–0.5808					0.14

better than the original Flory–Huggins equation for the ternary system with only one parameter.

We attempted to apply the temperature dependency to the modified Wilson model[19] for the correlation of water activity for binary and ternary aqueous polymer solutions. We used the following expressions, according to the suggestion of Wu et al.[27] which is specially used for polymer solutions:

$$\tau_{ji} = b\left(\frac{T_0}{T}\right) + c\left(\frac{T_0}{T}\right)^2 \qquad (9a)$$

$$\tau_{ij} = d\left(\frac{T_0}{T}\right) + e\left(\frac{T_0}{T}\right)^2 \qquad (9b)$$

where b, c, d, and e are adjustable model parameters and assumed to be temperature- and composition-independent. If the temperature range is not wide, we can fix $c = e$ as stated by Wu et al.[27] T_0 is equal to 273.15 K.

Therefore, we also fitted the experimental binary water activity data of Table 1 to eq 8 with a temperature dependency proposed by Wu et al.[27] (eq 9). The obtained parameters and ARD% (a_1) values are shown in Table 7 for the water (1) + PEGDME2000 (2) and water (1) + PPG400 (3) systems, respectively. As can be seen from Tables 5 and 7, we can conclude that the modified Wilson model in both forms (at each temperature and also with temperature dependency) is successful in representing binary activity data for both studied systems from dilute up to high concentration ranges.

We also checked the reliability of modified Wilson model for a ternary system studied in this work with temperature dependency. The parameters along with the absolute relative deviation for water activity are listed in Table 8. On the basis of ARD% values reported in Table 8, we conclude that this model works satisfactorily in the correlation of water activity for the studied ternary system at different temperatures.

■ CONCLUSIONS

The accurate water activity measurements have been carried out at T = (298.15, 308.15, and 318.15) K on water (1) + PEGDME2000 (2) + PPG400 (3) and their corresponding binary aqueous solutions. The data obtained were used to calculate vapor pressure solutions as a function of concentration. The effect of temperature on the VLE of binary and ternary systems has been studied. Furthermore, the activity results for binary and ternary aqueous solutions were correlated to the Flory–Huggins model from which the Flory interaction parameters χ_{12}, χ_{13} and χ_{23} were calculated. Negative χ_{23} values indicated strong attraction between segments of two polymers. Finally from the correlation of experimental water activity data for the binary and ternary polymer solutions with the modified Wilson model, it was found that this model has a good performance in representing VLE for the studied systems.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: 98 411 3340191. E-mail addresses: zafarani47@yahoo.com.

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