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Vapor Pressure of Acetonitrile + Polymer Binary Systems at 298.15 K

Rahmat Sadeghi*

Department of Chemistry, University of Kurdistan, Pasdaran Street, Sanandaj, Iran

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Vapor pressure data of six binary acetonitrile + polymer systems were determined experimentally using an improved isopiestic method at 298.15 K. Polymers were poly(ethylene glycol) 200, poly(ethylene glycol) 6000, poly(propylene glycol) 425, poly(propylene glycol) 1000, poly(vinylpyrrolidone) 10000, and poly(ethylene glycol) methaacrylate 360. Sodium iodide was used as the isopiestic standard for the determination of vapor pressures. The activities of acetonitrile in the polymer solutions were calculated from the vapor pressure data. Furthermore, the segment-based local composition models, NRTL, Wilson, NRF−NRTL, NRF−Wilson, and UNIQUAC were used to correlate the experimental vapor pressure and activity data.

Introduction

Vapor−liquid equilibria (VLE) in polymer + solvent systems are necessary for a variety of applications including surface acoustic-wave vapor sensors,[1,2] recovery of organic vapors from waste−air streams using a polymeric membrane,[3,4] pervaporation[5] and other polymeric membrane-separation processes, polymer devolatilization,[6] vapor-phase photografting,[7] and for optimum formulation of paints and coatings. For rational process and product design, experimental data correlations based on molecular thermodynamics are required.

VLE data for some polymer solutions have been compiled by Wohlfahrt.[8] In recent years, the vapor pressure data for some nonaqueous polymer solutions have been reported in the literature.[9−13] However, for acetonitrile + polymer systems a limited amount of experimental work has been carried out. In this respect, Gupta and Prausnitz[14] measured VLE data for acetonitrile with *cis*-1,4-polybutadiene, polyacrylonitrile, and poly(butadiene−*co*-acrylonitrile) solutions at 60 °C; but they have represented the results in figures without any experimental data. In the present report, vapor pressure of acetonitrile + poly(ethylene glycol) 200 (PEG_{200}), + PEG_{6000}, + poly(propylene glycol) 425 (PPG_{425}), + PPG_{1000}, + poly(ethylene glycol) methaacrylate 360 ($PEGMA_{360}$), and + poly(vinylpyrrolidone) 10000 (PVP_{10000}) are measured by the improved isopiestic method[15] at 298.15 K. The results were correlated with the segment-based local composition models NRTL,[16] Wilson,[17] NRF−NRTL,[16] NRF−Wilson,[18] and UNIQUAC.[19]

Experimental Procedure

Acetonitrile, sodium iodide, PEG_{200}, and PEG_{6000} were obtained from Merck; PPG_{425}, PPG_{1000}, PVP_{10000}, and $PEGMA_{360}$ were obtained from Aldrich. Sodium iodide (GR, minimum 99.5 %) was dried in an electrical oven at about 110 °C for 24 h prior to use. In this study, the isopiestic method was used to obtain the vapor pressure of acetonitrile + polymer systems. It is based on the phenomenon that different solutions, when connected through the vapor space, approach equilibrium by transferring solvent mass by distillation. Equilibrium was established once the temperature and pressure are uniform throughout the system, provided that no concentration gradients existed in the liquid phase. At equilibrium the chemical potentials of the solvent in each of the solutions in the closed system are identical. 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.[15] This apparatus consists of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard NaI + acetonitrile solutions, two flasks contained the polymer 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 equilibrium at (298.15 ± 0.01) K. The temperature was controlled to within ± 0.01 K. After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance with an uncertainty of $\pm 1 \times 10^{-7}$ kg. From the mass of each flask after equilibrium and the initial mass of salt and polymer, the mass fraction of each solution was calculated. The vapor pressure for the standard acetonotrile + NaI solutions at 298.15 K at different concentrations has been calculated from the correlation of Barthel and Lauermann.[20] It was assumed that the equilibrium condition was reached when the differences between the mass fractions of two standard solutions were less than 1 %. In all cases, averages of the duplicate are reported as the total isopiestic mass fraction. The uncertainty in the

Table 1. Experimental Isopiestic Mass Fractions *w*, Osmotic Coefficients ϕ, Activities of Acetonitrile a_1, and Vapor Pressures *p* for Acetonitrile (1) + PEG_{200} (2) at 298.15 K

w_{NaI}	w_2	ϕ_{NaI}	p/kPa	a_1
0.0000	0.0000	1.000	11.983	1.0000
0.0380	0.0850	0.760	11.781	0.9837
0.0457	0.1050	0.754	11.741	0.9804
0.0641	0.1530	0.743	11.643	0.9725
0.0686	0.1660	0.741	11.619	0.9705
0.0859	0.2081	0.734	11.525	0.9629
0.0974	0.2339	0.730	11.462	0.9578
0.1108	0.2670	0.726	11.386	0.9516
0.1271	0.2990	0.723	11.292	0.9440
0.1504	0.3490	0.719	11.152	0.9326
0.1736	0.3990	0.720	11.003	0.9205
0.1849	0.4186	0.721	10.926	0.9143

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* E-mail: rahsadeghi@yahoo.com or RSadeghi@uok.ac.ir. Tel/Fax: +98-871-6624133.

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Table 2. Experimental Isopiestic Mass Fractions *w*, Osmotic Coefficients ϕ, Activities of Acetonitrile a_1, and Vapor Pressures *p* for Acetonitrile (1) + PEG_{6000} (2) at 298.15 K

w_{NaI}	w_2	ϕ_{NaI}	p/kPa	a_1
0.0000	0.0000	1.000	11.983	1
0.0195	0.2306	0.788	11.877	0.9914
0.0264	0.2624	0.774	11.842	0.9886
0.0360	0.3004	0.762	11.792	0.9845
0.0427	0.3229	0.756	11.757	0.9817
0.0457	0.3322	0.754	11.741	0.9804
0.0530	0.3542	0.749	11.702	0.9773
0.0668	0.3810	0.742	11.629	0.9713
0.0810	0.4080	0.736	11.552	0.9651
0.0907	0.4268	0.732	11.499	0.9608
0.0980	0.4350	0.730	11.458	0.9575
0.1144	0.4580	0.725	11.366	0.9500
0.1345	0.4798	0.721	11.248	0.9405
0.1662	0.5116	0.719	11.052	0.9245
0.1972	0.5417	0.725	10.838	0.9071

Table 3. Experimental Isopiestic Mass Fractions *w*, Osmotic Coefficients ϕ, Activities of Acetonitrile a_1, and Vapor Pressures *p* for Acetonitrile (1) + PPG_{425} (2) at 298.15 K

w_{NaI}	w_2	ϕ_{NaI}	p/kPa	a_1
0.0000	0.0000	1.000	11.983	1
0.0190	0.0717	0.790	11.880	0.9917
0.0317	0.1225	0.767	11.814	0.9863
0.0363	0.1436	0.762	11.790	0.9844
0.0403	0.1619	0.758	11.769	0.9827
0.055	0.2176	0.748	11.692	0.9764
0.0610	0.2383	0.745	11.660	0.9738
0.0671	0.2570	0.742	11.627	0.9712
0.0686	0.2647	0.741	11.619	0.9705
0.0859	0.3157	0.734	11.525	0.9629
0.0942	0.3363	0.731	11.479	0.9592
0.1099	0.3800	0.726	11.391	0.9521
0.1265	0.4119	0.723	11.296	0.9443
0.1532	0.468	0.719	11.135	0.9312
0.1712	0.5017	0.719	11.019	0.9218
0.1818	0.524	0.721	10.948	0.9160
0.2091	0.5691	0.729	10.748	0.8998

Table 4. Experimental Isopiestic Mass Fractions *w*, Osmotic Coefficients ϕ, Activities of Acetonitrile a_1, and Vapor Pressures *p* for Acetonitrile (1) + PPG_{1000} (2) at 298.15 K

w_{NaI}	w_2	ϕ_{NaI}	p/kPa	a_1
0.0000	0.0000	1	11.983	1
0.0200	0.1548	0.787	11.875	0.9912
0.0363	0.2469	0.762	11.790	0.9844
0.0404	0.2694	0.758	11.769	0.9827
0.0668	0.3883	0.742	11.629	0.9713
0.0907	0.4655	0.732	11.499	0.9608
0.0980	0.4858	0.730	11.458	0.9575
0.1345	0.5538	0.721	11.248	0.9405

Table 5. Experimental Isopiestic Mass Fractions *w*, Osmotic Coefficients ϕ, Activities of Acetonitrile a_1, and Vapor Pressures *p* for Acetonitrile (1) + $PEGMA_{360}$ (2) at 298.15 K

w_{NaI}	w_2	ϕ_{NaI}	p/kPa	a_1
0.0000	0.0000	1.000	11.983	1
0.0177	0.0641	0.794	11.886	0.9922
0.0264	0.0967	0.774	11.842	0.9886
0.0363	0.1310	0.762	11.790	0.9844
0.0427	0.1469	0.756	11.757	0.9817
0.0457	0.1491	0.754	11.741	0.9804
0.0550	0.1736	0.748	11.692	0.9764
0.0693	0.2098	0.741	11.615	0.9702
0.0820	0.2375	0.735	11.547	0.9647
0.0907	0.2565	0.732	11.499	0.9608
0.0980	0.2724	0.730	11.458	0.9575
0.1149	0.3125	0.725	11.363	0.9497
0.1345	0.3525	0.721	11.248	0.9405
0.1544	0.3884	0.719	11.127	0.9306
0.1736	0.4198	0.720	11.003	0.9205
0.1849	0.4360	0.721	10.926	0.9143
0.1972	0.4518	0.725	10.838	0.9071

Table 6. Experimental Isopiestic Mass Fractions *w*, Osmotic Coefficients ϕ, Activities of Acetonitrile a_1, and Vapor Pressures *p* for Acetonitrile (1) + PVP_{10000} (2) at 298.15 K

w_{NaI}	w_2	ϕ_{NaI}	p/kPa	a_1
0.0000	0.0000	1.000	11.983	1
0.0150	0.1953	0.804	11.900	0.9933
0.0258	0.3266	0.775	11.845	0.9888
0.0264	0.3308	0.774	11.842	0.9886
0.0317	0.3889	0.767	11.814	0.9863
0.0345	0.4236	0.763	11.800	0.9852
0.0399	0.4669	0.758	11.771	0.9829
0.0427	0.4866	0.756	11.757	0.9817
0.0516	0.5254	0.750	11.710	0.9779
0.0552	0.5369	0.748	11.691	0.9764
0.0660	0.5596	0.742	11.633	0.9717
0.0671	0.5627	0.742	11.627	0.9712
0.0686	0.5677	0.741	11.619	0.9705
0.0859	0.6041	0.734	11.525	0.9629
0.0974	0.6243	0.730	11.462	0.9578
0.1140	0.6528	0.725	11.368	0.9502
0.1271	0.6671	0.723	11.292	0.9440
0.1532	0.6900	0.719	11.135	0.9312
0.1677	0.7066	0.719	11.042	0.9237
0.1818	0.7230	0.721	10.948	0.9160
0.1972	0.7370	0.725	10.838	0.9071

Table 7. Molar Volume $V_1°$, Vapor Pressure $p°$, Second Virial Coefficient *B*, Density $\rho_1°$, and Molecular Weight M_1 of Acetonitrile[a]

$10^6\,V_1°/\mathrm{m^3{\cdot}mol^{-1}}$	$p°$/kPa	$10^6 B/\,\mathrm{m^3{\cdot}mol^{-1}}$	$\rho_1°/\mathrm{kg{\cdot}m^{-3}}$	$M_1/\mathrm{kg{\cdot}mol^{-1}}$
52.85	11.983	−6190	776.75	0.041052

[a] Taken from ref 20.

measurement of vapor pressure was estimated to be ± 0.002 Pa.

Results and Discussion

Experimental Results. Barthel and Lauermann[20] obtained the following polynomial equation for vapor pressure (p) of acetonotrile + NaI solutions at 298.15 K as a function of molality m:

$$p/\mathrm{Pa} = 11982.8 - 0.047493 - 5.674806\left(\frac{m}{m°}\right) + 0.467791\left(\frac{m}{m°}\right)^2 - 0.002642\left(\frac{m}{m°}\right)^3 - 0.066637\left(\frac{m}{m°}\right)^4 \quad (1)$$

where $m° = 1\ \mathrm{mol{\cdot}kg^{-1}}$. The precision of the fitting parameters permits this polynomial to be used to calculate p at concentrations range (0.06 to 1.54) $\mathrm{mol{\cdot}kg^{-1}}$ at an uncertainty of better than 0.4000 Pa.[20] At isopiestic equilibrium, the vapor pressure of all solutions within the isopiestic system is identical. Therefore, the isopiestic equilibrium mass fractions (w) with reference standard solutions of NaI in acetonitrile as reported in Tables 1 to 6 enabled the calculation of the vapor pressure in the solutions of acetonitrile (1) + polymer (2) from that of reference solutions. The obtained vapor pressure data for the investigated acetonitrile (1) + polymer (2) systems are given in Tables 1 to 6. From the vapor pressure data, the solvent activity data of solutions (a_1) were determined with the help of the following equation:

$$\ln(a_1) = \ln\left(\frac{p}{p°}\right) + \frac{(B - V_1°)(p - p°)}{RT} \quad (2)$$

where B, $V_1°$, and $p°$ are the second virial coefficient, molar

Table 8. Parameters of the NRTL, Wilson, NRF−NRTL, Equations along with the Corresponding Absolute Relative Percentage Deviations (ARD)

	NRTL			Wilson			NRF−NRTL		
system	τ_{12}	τ_{21}	100 ARD	$E_{12} \times 10^{-4}$	$E_{21} \times 10^{-4}$	100 ARD	τ_{12}	τ_{21}	100 ARD
acetonitrile (1) + PEG_{200} (2)	2.7062	−1.7125	1.25(1.28)[a]	2.0426	−1.4798	1.25(1.28)	1.8417	−0.3911	1.28(1.28)
acetonitrile (1) + PEG_{6000} (2)	2.7062	−1.7125	1.04(1.08)	2.0426	−1.4798	1.05(1.08)	1.8417	−0.3911	1.08(1.08)
acetonitrile (1) + PPG_{425} (2)	−0.4727	1.2247	0.12(0.12)	−0.7582	1.0649	0.12(0.12)	−5.4194	−2.3960	1.00(1.04)
acetonitrile (1) + PPG_{1000} (2)	−0.4727	1.2247	0.22(0.23)	−0.7582	1.0649	0.22(0.23)	−5.4194	−2.3960	1.17(1.20)
acetonitrile (1) + PEGMA360(2)	−0.2145	0.5170	0.06(0.06)	−0.3692	0.4709	0.06(0.06)	−1.4755	0.0561	0.28(0.28)
acetonitrile (1) + PVP_{1000} (2)	−0.6197	1.4738	0.18(0.18)	−0.8845	1.2550	0.18(0.19)	−108.512	108.116	0.94(0.97)

[a] The deviations in parenthesis are related to the vapor pressure data.

Table 9. Parameters of the NRF−Wilson and UNOQUAC Equations along with the Corresponding Absolute Relative Percentage Deviations (ARD)

	UNIQUAC			NRF−Wislon		
system	τ_{12}	τ_{21}	100 ARD	$E_{12} \times 10^{-4}$	$E_{21} \times 10^{4}$	100 ARD
acetonitrile (1) + PEG_{200} (2)	2.0015	−1.0234	1.37(1.41)	−1.3797	0.6568	1.34(1.38)
acetonitrile (1) + PEG_{6000} (2)	2.0015	−1.0234	1.14(1.18)	−1.3797	0.6568	1.11(1.15)
acetonitrile (1) + PPG_{425} (2)	0.4398	0.4815	0.06(0.07)	0.8547	0.0158	2.22(2.27)
acetonitrile (1) + PPG_{1000} (2)	0.4398	0.4815	0.14(0.14)	0.8547	0.0158	2.74(2.82)
acetonitrile (1) + PEGMA360 (2)	0.5402	−0.1158	0.06(0.06)	−0.8263	0.0548	0.32(0.33)
acetonitrile (1) + PVP_{1000} (2)	0.3797	0.6396	0.20(0.21)	−0.4207	0.0286	6.81(6.98)

volume, and vapor pressure of pure acetonitrile, respectively. R is the gas constant, and T is the absolute temperature. The values of the physical properties for the acetonitrile are summarized in Table 7. The experimental acetonitrile activity data are also given in Tables 1 to 6. The uncertainty in the measurement of acetonitrile activity was estimated to be ± 0.002. The measured vapor pressure and solvent activity data for investigated acetonitrile + polymer solutions are shown in Figures 1 and 2, respectively. As can be seen from Figures 1 and 2, in the same polymer mass fraction the magnitudes of the both vapor pressure and acetonitrile activity have the order of PVP_{10000} > PEG_{6000} > PPG_{1000} > PPG_{425} > $PEGMA_{360}$ > PEG_{200}. In fact, the solvent absorption of a polymer increases with a decrease in the molecular weight of the polymer. In the case of PEG, PPG, and PEGMA, this behavior is mainly attributed to the attraction between the end group (OH) of the polymer and the polar end group (CN) of the solvent. In Figure 3, vapor pressure depression of PVP_{10000} in various solvents has been shown at 298.15 K. As can be seen from Figure 3, vapor pressure depression in the small alcohols is larger than those in the acetonitrile. This behavior is may be attributed to the strong hydrogen bond interaction between the OH group of small alcohols and the imide group of PVP. This behavior is also observed for PPG, PEG, and PEGMA.

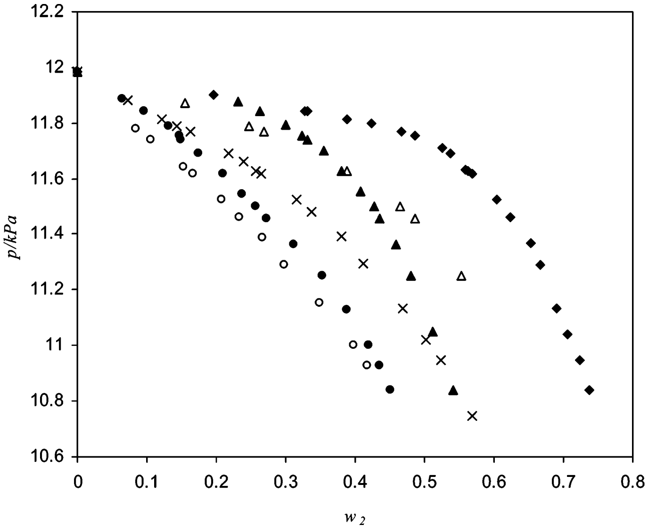

Figure 1. Vapor pressure data for acetonitrile (1) + polymer (2) at 298.15 K: ○, PEG_{200}; ●, $PEGMA_{360}$; ×, PPG_{425}; △, PPG_{1000}; ▲, PEG_{6000}; ■, PVP_{10000}.

Correlation of Data. In this work, for the correlation of solvent activity for the investigated systems the segment-based local composition models NRTL,[16] Wilson,[17] NRF−NRTL,[16] NRF−Wilson,[18] and UNIQUAC[19] were considered. In all of these models, the activity coefficient of the solvent (1) is considered as the sum of the combinatorial, ln γ_1^{Comb}, and the residual contribution, ln γ_1^{Res}:

$$\ln \gamma_1 = \ln \gamma_1^{\mathrm{Comb}} + \ln \gamma_1^{\mathrm{Res}} \tag{3}$$

In this work, for all of the models the Freed correction to the Flory−Huggins expression[21] was used for the combinatorial contribution, and the NRTL, Wilson, NRF−NRTL, NRF−Wilson, and UNIQUAC models were used for the residual contribution.

Freed Flory−Huggins Combinatorial Term. The Freed Flory−Huggins combinatorial term is the exact solution for the Flory−Huggins lattice theory. It is expressed as a polynomial expansion in powers of a non-randomness factor (α). Freed only used the first-order correction:

$$\ln \gamma_1^{\mathrm{Comb}} = \ln \frac{\phi_1}{x_1} + \left(1 - \frac{r_1}{r_2}\right)\phi_2 + \alpha\left(\frac{1}{r_1} - \frac{1}{r_2}\right)^2 \phi_2^{\,2} \tag{4}$$

where the first and second terms on the right-hand side of eq 4 account for the contribution for the excess entropy associated with random mixing and is the same as the expression in Flory−Huggins theory. The third term is the correction to the Flory−Huggins theory and may be understood as the local composition effect from the chained segments in a polymer. In this equation

$$\phi_i = \frac{r_i n_i}{r_1 n_1 + r_2 n_2} \tag{5}$$

In these relations, n_i and x_i are the number of moles and the mole fraction of the component i, respectively. r_i is the number of the segment in the component i.

NRTL Residual Term:

$$\frac{1}{r_1}\ln\gamma_1^{\mathrm{NRTL}} = \phi_2^{\,2}\left(\frac{\tau_{21}\exp(-\alpha\tau_{21})^2}{(\phi_1+\phi_2\exp(-\alpha\tau_{21}))^2} + \frac{\tau_{12}\exp(-\alpha\tau_{12})}{(\phi_2+\phi_1\exp(-\alpha\tau_{12}))^2}\right) \qquad (6)$$

where the NRTL parameters τ_{ij} are fitted to the experimental data.

Wilson Residual Term:

$$-\frac{1}{Cr_1}\ln\gamma_1^{\mathrm{Wilson}} = \ln\left(\phi_1+\phi_2\exp\left(-\frac{E_{21}}{CRT}\right)\right) + \phi_1\left(\frac{1-\left(\phi_1+\phi_2\exp\left(-\frac{E_{21}}{CRT}\right)\right)}{\phi_1+\phi_2\exp\left(-\frac{E_{21}}{CRT}\right)}\right) + \phi_2\left(\frac{\exp\left(-\frac{E_{12}}{CRT}\right)-\left(\phi_2+\phi_1\exp\left(-\frac{E_{12}}{CRT}\right)\right)}{\phi_2+\phi_1\exp\left(-\frac{E_{12}}{CRT}\right)}\right) \qquad (7)$$

where C is a parameter that represents the effective coordination number in the system, and the Wilson parameters, E_{ij}, are fitted to the experimental data.

NRF−NRTL Residual Term:

$$\frac{1}{r_1}\ln\gamma_1^{\mathrm{NRF-NRTL}} = \phi_2^{\,2}\left(\frac{\tau_{21}\exp(-\alpha\tau_{21})^2}{(\phi_1+\phi_2\exp(-\alpha\tau_{21}))^2} + \frac{\tau_{12}\exp(-\alpha\tau_{12})}{(\phi_2+\phi_1\exp(-\alpha\tau_{12}))^2}\right) + (\phi_1-1)(\phi_2\tau_{12}+\phi_2\tau_{21}) \qquad (8)$$

NRF−Wilson Residual Term:

$$-\frac{1}{Cr_1}\ln\gamma_1^{\mathrm{NRF-Wilson}} = \ln\left(\phi_1+\phi_2\exp\left(-\frac{E_{21}}{CRT}\right)\right) + \phi_1\left(\frac{1-\left(\phi_1+\phi_2\exp\left(-\frac{E_{21}}{CRT}\right)\right)}{\phi_1+\phi_2\exp\left(-\frac{E_{21}}{CRT}\right)}\right) + \phi_2\left(\frac{\exp\left(-\frac{E_{12}}{CRT}\right)-\left(\phi_2+\phi_1\exp\left(-\frac{E_{12}}{CRT}\right)\right)}{\phi_2+\phi_1\exp\left(-\frac{E_{12}}{CRT}\right)}\right) + \phi_2^{\,2}\left(\frac{E_{12}}{CRT}+\frac{E_{21}}{CRT}\right) \qquad (9)$$

UNIQUAC Residual Term:

$$\ln\gamma_1^{\mathrm{UNIQAC}} = -q_1\ln(X_1+X_2\tau_{21}) + q_1X_2\left(\frac{\tau_{21}}{X_1+X_2\tau_{21}} - \frac{\tau_{12}}{X_2+X_1\tau_{12}}\right) \qquad (10)$$

$$X_i = \frac{q_in_i}{q_1n_1+q_2n_2} \qquad (11)$$

$$q_{\mathrm{i}} = r_{\mathrm{i}}\left(1-2\alpha\left(1-\frac{1}{r_{\mathrm{i}}}\right)\right) \qquad (12)$$

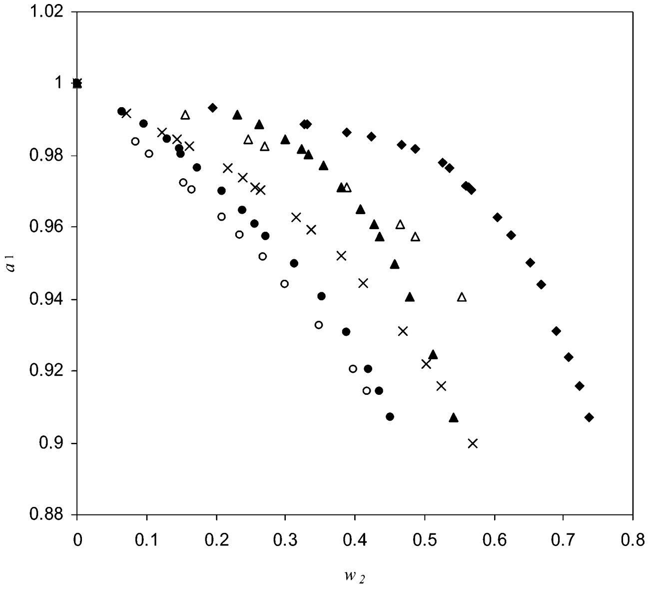

Figure 2. Solvent activity data for acetonitrile (1) + polymer (2) at 298.15 K: ○, PEG$_{200}$; ●, PEGMA$_{360}$; ×, PPG$_{425}$; △, PPG$_{1000}$; ▲, PEG$_{6000}$; ■, PVP$_{10000}$.

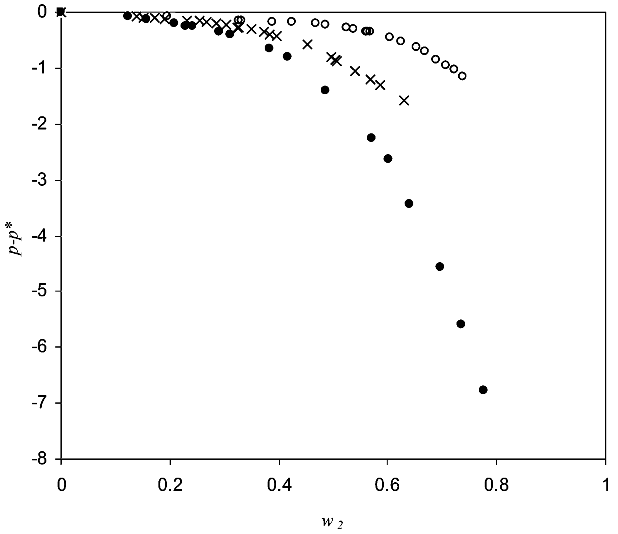

Figure 3. Vapor pressure depression of PVP$_{10000}$ in various solvents at 298.15 K: ●, methanol (ref 12); ×, ethanol (ref 12); ○, acetonitrile.

A value of $r = 1$ was used for solvents, and for a polymer the value of r is the ratio of the molar volume of polymer to that of the solvent at 298.15 K. The molar volumes of polymers have been calculated from the specific volumes and the number average molar masses of polymers. The specific volume of PEG, PPG, PVP, and PEGMA at 298.15 K are 0.838,[22] 0.997,[23] 0.799,[24] and 0.9165.[13] The values of non-randomness factor α and effective coordination number C were set to 0.25[25] and 10,[26] respectively. The segment-based local composition models NRTL, Wilson, NRF−NRTL, NRF−Wilson, and UNIQUAC were used for the correlation of the experimental solvent activity and vapor pressure data, and the obtained parameters for the studied systems are presented in Tables 8 and 9 along with the corresponding absolute relative percentage deviations (ARD %) of the fit. On the basis of the deviations given in Tables 8 and 9, we conclude that the segment-based local composition models NRTL, Wilson, and UNIQUAC have similar behavior in the correlation of obtained experimental solvent activity and vapor pressure data and that their results are better than the NRF−NRTL and NRF−Wilson models. In the NRTL, Wilson, and UNIQUAC models, the references states are pure liquid for solvent and a hypothetical segment aggregate state for segments of polymer, but the references states for the NRF−NRTL and NRF−Wilson models are the random case for all the species. In fact the only difference between the NRTL and NRF−NRTL models (also between the Wilson and NRF−Wilson models) is in their references states. Therefore, it seems that for the systems investigated in this work, the models that use the pure liquid for reference state of species produce better results than the models that use the random case for the reference state of species.

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