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Vapor Pressure Osmometry Determination of Solvent Activities of Different Aqueous and Nonaqueous Polymer Solutions at 318.15 K

Rahmat Sadeghi*,† and Yasaman Shahebrahimi‡

†Department of Chemistry, University of Kurdistan, Sanandaj, Iran

‡Department of Chemical Engineering, University of Kurdistan, Sanandaj, Iran

ABSTRACT: Vapor−liquid equilibria (VLE) measurements have been performed for several binary polymer + solvent systems at 318.15 K using a vapor pressure osmometry (VPO) method in the semidiluted polymer concentration range. The polymers were poly(ethylene oxide) dimethyl ether 250, poly(ethylene oxide) dimethyl ether 500, poly(ethylene oxide) dimethyl ether 2000, poly(ethylene oxide) 400, and poly(propylene oxide) 400, and the investigated solvents were water, methanol, ethanol, acetonitrile, and 2-propanol. The variations of the activity of solvents with the polymer molar mass and type of polymer and solvent were investigated, and the results have been interpreted in terms of the solvent/polymer interactions. In the second part of this work, the segment-based local composition models, nonrandom two-liquid (NRTL) and Wilson, as well as the Flory−Huggins model were used to correlate the experimental activity data.

1. INTRODUCTION

A quantitative description of vapor−liquid equilibria (VLE) behavior of polymer solutions is necessary for a variety of applications such as 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] optimum formulation of paints and coatings, functionalization of nanoparticles in aqueous media,[8,9] and formation of nanocomposites.[10,11] 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.[12] Although water activity data for some aqueous or nonaqueous polymer solutions have been reported in the literature,[13−33] however, similar information on the vapor−liquid equilibria of solutions of poly(ethylene oxide) dimethyl ethers (PEODME) is scarce.[34,35] In continuation of our previous work,[35] in the present report, the activities of water, methanol, ethanol, acetonitrile, and 2-propanol in poly(ethylene oxide) 400 (PEO400), PEODME250, PEODME500, PEODME2000, and poly(propylene oxide) 400 (PPO400) solutions have been measured by the vapor pressure osmometry (VPO) method at 318.15 K.

As mentioned, accurate modeling of phase behavior of polymer + solvent systems is required for the proper design of separation processes such as the removal of low-molecular weight substances from polymers by devolatilization or polymer fractionation.[36] There are two categories of models available for description of thermodynamic properties of polymer solutions.[36] The activity coefficient, or excess Gibbs energy (G^{ex}) models, and the equation of state (EOS) models. One of the most important class of G^{ex} models for phase equilibrium calculations of polymer solutions are those of segment-based local composition models[37−42] which use a combination of the Flory−Huggins expression for the configurational entropy of mixing molecules of different sizes and a segment-based local composition model such as the nonrandom two-liquid (NRTL),[37−39] nonrandom factor (NRF),[39,40] and Wilson[41] models to account for the energetic interactions between solvent molecules and segments of polymer. The segment-based models provide the most flexible and convenient thermodynamic framework for researchers to characterize the nonideal behavior of polymer solutions. In short, it is most desirable to associate the nonideality of a solvent−polymer mixture with solvent−segment interaction parameters, rather than with the solvent−polymer interaction parameters or the solvent−functional group interaction parameters. The advantage of the segment-based models over conventional models for the correlation of polymer solution experimental data is that, unlike the classical models, they can cover a wide range of polymer molar masses with a series of interaction parameters, which provides a predictive capability. In the second part of this work, the segment-based local composition models, NRTL[39] and Wilson,[41] as well as the Flory−Huggins model[43,44] were used to correlate the experimental activity data.

2. EXPERIMENTAL PROCEDURE

Sodium chloride, lithium bromide, PEODME250, PEODME500, PEODME2000, PEO400, acetonitrile, methanol, ethanol, and 2-propanol were obtained from Merck, and PPO400 was obtained from Fluka. Sodium chloride and lithium bromide were dried in an electrical oven at about 110 °C for 24 h prior to use.

In this study, the VPO method was used to obtain the solvent activities of the investigated polymer solutions. VPO was performed with the help of an Osmomat K-7000 (Knauer Inc.). The method and procedure have been described in detail in a previous paper.[35] First, the instrument was calibrated using aqueous NaCl or nonaqueous LiBr solutions as a reference with known osmotic coefficients in the proper concentration range, yielding a function that correlates the panel readings to the corresponding concentrations of the reference solutions and therefore their osmotic

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Table 1. Activity of Solvent (a_1) and Vapor Pressure (p) for Different Water (1) + Polymer (2) Systems Obtained from the VPO Method at 318.15 K

w_2	a_1	p/kPa	w_2	a_1	p/kPa	w_2	a_1	p/kPa
Water (1) + PEODME250 (2)			Water (1) + PEODME500 (2)			Water (1) + PEODME2000 (2)		
0.0100	0.9994	9.584	0.0118	0.9991	9.581	0.0301	0.9995	9.585
0.0251	0.9988	9.578	0.0301	0.9988	9.578	0.0578	0.9991	9.581
0.0304	0.9983	9.573	0.0499	0.9985	9.575	0.0901	0.9981	9.571
0.0496	0.9974	9.565	0.0503	0.9984	9.574	0.0992	0.9977	9.568
0.0498	0.9972	9.563	0.0734	0.9972	9.563	0.1197	0.9973	9.564
0.0721	0.9955	9.546	0.1007	0.9959	9.550	0.1515	0.9962	9.553
0.0819	0.9950	9.542	0.1208	0.9951	9.543	0.1791	0.9953	9.544
0.0954	0.9935	9.527	0.1488	0.9934	9.526	0.1976	0.9940	9.532
0.0999	0.9932	9.524	0.1604	0.9927	9.519	0.2109	0.9936	9.528
0.1152	0.9918	9.511	0.1776	0.9908	9.501	0.2454	0.9914	9.507
0.1355	0.9898	9.492	0.2053	0.9893	9.487	0.2734	0.9900	9.493
0.1413	0.9897	9.491	0.2486	0.9855	9.450	0.2869	0.9891	9.485
0.1461	0.9891	9.485	0.2700	0.9833	9.429	0.2964	0.9869	9.464
0.1654	0.9873	9.467	0.2960	0.9806	9.403	0.3298	0.9831	9.427
0.1973	0.9840	9.436	0.3165	0.9777	9.375	0.3417	0.9821	9.417
0.2249	0.9809	9.406				0.3605	0.9796	9.393
0.2430	0.9788	9.386						
Water (1) + PEO400 (2)			Water (1) + PPO400 (2)					
0.0250	0.9992	9.582	0.0481	0.9981	9.571			
0.0277	0.9986	9.576	0.1014	0.9963	9.554			
0.0496	0.9976	9.567	0.1505	0.9943	9.535			
0.0604	0.9972	9.563	0.1981	0.9930	9.522			
0.0990	0.9946	9.538	0.2023	0.9929	9.521			
0.0991	0.9951	9.543	0.3006	0.9910	9.503			
0.1297	0.9927	9.519	0.3010	0.9909	9.502			
0.1493	0.9913	9.506	0.3818	0.9900	9.493			
0.1600	0.9910	9.503	0.3990	0.9896	9.490			
0.1753	0.9898	9.492	0.4879	0.9882	9.476			
0.1835	0.9891	9.485	0.5040	0.9881	9.475			
0.1987	0.9870	9.465	0.5803	0.9874	9.468			
0.2268	0.9845	9.441	0.5998	0.9870	9.465			
			0.7069	0.9847	9.442			

coefficients. Then in the same conditions, the panel readings were measured for the studied polymer solutions. For each solution, at least five determinations (zero point adjustment and new solution) were performed, and the mean value is reported. Generally, the deviations from the mean value were less than 1 %. The cell temperature, which is electronically controlled, has a standard uncertainty of $\pm 1 \cdot 10^{-3}$ K. The solvent activities for the reference NaCl + water,[45] LiBr + methanol,[46] ethanol,[47] acetonitrile,[48] and 2-propanol[49] solutions at different concentrations have been calculated from the correlation given in the corresponding literature.

For a certain polymer solution which has a same instrument reading as a reference solution with molality m_{ref} and osmotic coefficient Φ_{ref}, the solvent activity a_1 was obtained according to:

$$a_1 = \exp(-0.001\nu_{\text{ref}} m_{\text{ref}} \Phi_{\text{ref}} M_1) \qquad (1)$$

where ν_{ref} is the stoichiometric number of reference electrolyte and M_1 is the molar mass of the solvent. Φ_{ref} is the osmotic coefficient for the reference solution with molality m_{ref}. The uncertainty in the measurement of solvent activity was found to be better than $\pm 2 \cdot 10^{-4}$.

3. RESULTS AND DISCUSSION

3.1. Experimental Results. Tables 1 to 5 show the experimental solvent activity data of the investigated polymer solutions obtained with the help of the osmometer (VPO technique) at 318.15 K. From the solvent activity data, the vapor pressure data of solutions, p, were determined with the help of the following equation:[46−49]

$$\ln(a_1) = \ln\left(\frac{p}{p^\circ}\right) + \frac{(B - V_1^\circ)(p - p^\circ)}{RT} \qquad (2)$$

where B, V_1°, and p° are the second virial coefficient, molar volume, and vapor pressure of pure solvent, respectively. R is the gas constant, and T is the absolute temperature. The calculated vapor pressure data of the investigated polymer solutions are also

Table 2. Activity of Solvent (a_1) and Vapor Pressure (p) for Different Methanol (1) + Polymer (2) Systems Obtained from the VPO Method at 318.15 K

w_2	a_1	p/kPa	w_2	a_1	p/kPa	w_2	a_1	p/kPa
Methanol (1) + PEODME250 (2)			Methanol (1) + PEODME500 (2)			Methanol (1) + PEODME2000(2)		
0.0095	0.9983	44.473	0.0249	0.998	44.459	0.0489	0.9978	44.450
0.0249	0.9966	44.395	0.0394	0.9966	44.395	0.0741	0.9962	44.377
0.0396	0.9940	44.277	0.0596	0.995	44.322	0.1001	0.9948	44.313
0.0601	0.9905	44.118	0.0803	0.9930	44.231	0.1473	0.9914	44.158
0.0807	0.9878	43.995	0.1002	0.9905	44.118	0.2109	0.9876	43.986
0.1000	0.9841	43.826	0.1252	0.9881	44.008	0.2493	0.9837	43.808
0.1196	0.9810	43.685	0.1506	0.9854	43.885	0.2909	0.9791	43.599
			0.1745	0.9825	43.753			
			0.1948	0.9797	43.626			
Methanol (1) + PEO400 (2)			Methanol (1) + PPO400 (2)					
0.0197	0.9982	44.468	0.0178	0.9981	44.463			
0.0295	0.9970	44.413	0.0301	0.9969	44.409			
0.0497	0.9949	44.318	0.0527	0.9947	44.309			
0.0694	0.9926	44.213	0.0702	0.9926	44.213			
0.0890	0.9901	44.099	0.0903	0.9901	44.099			
0.1103	0.9869	43.954	0.1106	0.9876	43.986			
0.1338	0.9844	43.840	0.1343	0.9848	43.858			
0.1603	0.9800	43.640	0.1594	0.9811	43.690			

Table 3. Activity of Solvent (a_1) and Vapor Pressure (p) for Different Ethanol (1) + Polymer (2) Systems Obtained from the VPO Method at 318.15 K

w_2	a_1	p/kPa	w_2	a_1	p/kPa	w_2	a_1	p/kPa
Ethanol (1) + PEODME250 (2)			Ethanol (1) + PEODME500 (2)			Ethanol (1) + PEO400 (2)		
0.0101	0.9978	22.99	0.0098	0.9987	23.012	0.0102	0.9984	23.005
0.0267	0.9951	22.927	0.0247	0.9972	22.976	0.0248	0.9967	22.965
0.0478	0.9918	22.850	0.0495	0.9952	22.930	0.0507	0.9937	22.894
0.0611	0.9891	22.787	0.0692	0.9929	22.876	0.0800	0.9900	22.808
0.0807	0.9856	22.705	0.0979	0.9895	22.796	0.1054	0.9864	22.723
0.0951	0.9823	22.627	0.1266	0.9860	22.714	0.1277	0.9826	22.634
0.1096	0.9789	22.548	0.1504	0.9823	22.627	0.1531	0.9777	22.520
			0.1713	0.9795	22.562			
Ethanol (1) + PPO400 (2)								
0.0099	0.9985	23.007						
0.0298	0.9960	22.948						
0.0483	0.9941	22.904						
0.0694	0.9916	22.845						
0.0889	0.9888	22.780						
0.1139	0.9850	22.691						
0.1394	0.9791	22.553						

given in Tables 1 to 5. The uncertainty in the determination of vapor pressure was found to be about $\pm 2 \cdot 10^{-3}$ kPa.

In Figure 1, comparisons of the experimental water activity data measured in this work with those taken from the literature obtained by the isopiestic method have been made for aqueous PPO400 solutions at 318.15 K. As can be seen, there is a good agreement between the results obtained in this work and those taken from the literature. Figures 2 and 3 respectively show the measured solvent activity data for the investigated water + polymer and acetonitrile + polymer systems at 318.15 K. The other systems investigated in this work have a similar behavior with the acetonitrile + polymer system. As can be seen, the solvent activity of a polymer solution increases as the polymer molar mass decreases. In fact, the results are in consistent with the valid thermodynamic facts that, in a highly dilute solution of a nonvolatile solute, the activity of the volatile solvent at a given mass concentration of solute is inversely proportional to the molar mass of the solute, and this fact forms a basis for the molar mass determination by VPO. Figure 2 shows that, for high polymer concentration ($0.23 < w_2$), in the same polymer mass

Table 4. Activity of Solvent (a_1) and Vapor Pressure (p) for Different 2-Propanol (1) + Polymer (2) Systems Obtained from the VPO Method at 318.15 K

w_2	a_1	p/kPa	w_2	a_1	p/kPa	w_2	a_1	p/kPa
2-Propanol (1) + PEODME250 (2)			2-Propanol (1) + PEODME500 (2)			2-Propanol (1) + PEO400 (2)		
0.0099	0.9978	18.115	0.0099	0.9985	18.127	0.0099	0.9983	18.124
0.0199	0.9957	18.076	0.0247	0.9969	18.098	0.0249	0.9961	18.083
0.0300	0.9932	18.030	0.0417	0.9951	18.065	0.0500	0.9927	18.021
0.0495	0.9892	17.956	0.0594	0.9930	18.026	0.0798	0.9879	17.932
0.0596	0.9866	17.909	0.0793	0.9904	17.978	0.1057	0.9835	17.852
0.0802	0.9821	17.826	0.0970	0.9873	17.921	0.1350	0.9790	17.769
0.0935	0.9795	17.778	0.1203	0.9843	17.866	0.1518	0.9759	17.712
0.1029	0.9773	17.738	0.1498	0.9808	17.802			
0.1092	0.9765	17.723	0.1799	0.9783	17.756			
2-Propanol (1) + PPO400 (2)								
0.0102	0.9981	18.120						
0.0251	0.9959	18.080						
0.0400	0.9941	18.046						
0.0603	0.9905	17.980						
0.0791	0.9876	17.927						
0.0994	0.9837	17.855						
0.1249	0.9786	17.761						
0.1391	0.9762	17.717						

fraction the magnitudes of the water activity have the order of PPO400 > PEODME2000 > PEODME500 > PEO400 > PEODME250. However, for low polymer concentration ($w_2 < 0.23$), the water activities of the investigated polymer solutions follow the order PEODME2000 > PEODME500 ≈ PPO400 > PEO-400 > PEODME250. The polymers PEO and PEODME have similar repeating units and therefore for a certain polymer mass fraction and polymer molar mass, the same water activity values for aqueous solutions of PEO and PEODME may be expected. However, PPO contains a greater proportion of hydrocarbon in its molecule and also the side chain methyl groups in PPO hinder hydrogen bonding between water molecules and the ether oxygen atoms. Gunninghame and Malcolm[50] showed that the heat of mixing with water per mole of glycol is more negative for PEO than for PPO. In contrast to PEO and PEODME, the solvability between water and PPO is very low so that PPO400 is water insoluble in very wide concentration range when the temperature is higher than about 54 °C.[14] The larger negative slope of the a_1 against w_2 at high polymer mass fraction is attributed to extensive hydrogen bonding of water molecules to the polymer, and the smaller negative slopes at low polymer mass fraction suggest that hydrophobic hydration of the polymer is an important factor in its dilute solution behavior.[35] The polymer concentration range in which the hydrophobic hydration of the polymer is a dominant factor increases by increasing polymer molar mass. PPO because of greater proportion of hydrocarbon in its molecule has a greater polymer concentration range in which the hydrophobic hydration of the polymer is an important factor in relative to other investigated polymers. As can be seen from Figure 1, for aqueous solutions of PPO with $w_2 < 0.8$, the hydrophobic hydration of the polymer is an important factor. However, for aqueous solutions of PPO with $w_2 > 0.8$, the hydrophilic hydration of the polymer is an important factor.

As can be seen from Figure 3, the solvent activities of the investigated nonaqueous polymer solutions in the whole polymer concentration range follow the order PEODME2000 > PEODME500 > PEO400 ≈ PPO400 > PEODME250, which implies that the effect of the solute on solvent activity decreases as solute molar mass rises. In Figures 4 and 5, respectively, the variations of the solvent activity and vapor pressure depression as a function of polymer mass fraction for solutions of PEODME500 in different solvents investigated in this work have been shown. A similar behavior was observed for other investigated polymers. As can be seen, for polymer mass fractions smaller than about 0.09, the magnitudes of the measured solvent activity and vapor pressure depression data respectively follow the order 2-propanol < acetonitrile ≈ ethanol < methanol < water and methanol > acetonitrile > ethanol > 2-propanol > water. However, for the polymer mass fractions higher than about 0.09, the magnitudes of the measured solvent activity and vapor pressure depression data respectively follow the order acetonitrile < 2-propanol < ethanol < methanol < water and acetonitrile > methanol > ethanol >2-propanol > water. The vapor pressures of pure solvents, $p°$, for methanol, acetonitrile, ethanol, 2-propanol, and water at $T = 318.15$ K are (44.550, 27.758, 23.042, 18.155, and 9.590) kPa, respectively. From the plots of vapor pressure depression, it would be expected that, at high polymer concentrations, the polymer−solvent interaction follows the sequence water < 2-propanol < ethanol < methanol < acetonitrile.

A comparison between the data obtained in this work and those obtained in our previous works[21,23,35] shows that water activities of the water + polymer systems increase with increasing temperature and by increasing temperature, the increase of vapor pressure of polymer + H_2O solution is larger than those of pure water. This is because the polymers become more hydrophobic with increasing temperature. However the results obtained in this work and those obtained in the references[31,32] show that, at any mass fraction, as the temperature is increased the solvent activity values are decreased, indicating an increase of interaction between polymer and nonaqueous solvents as the temperature is increased. Similarly, it has been found that the values of the

Table 5. Activity of Solvent (a_1) and Vapor Pressure (p) for Different Acetonitrile (1) + Polymer (2) Systems Obtained from the VPO Method at 318.15 K

w_2	a_1	p/kPa	w_2	a_1	p/kPa	w_2	a_1	p/kPa
Acetonitrile (1) + PEODME250 (2)			Acetonitrile (1) + PEODME500 (2)			Acetonitrile (1) + PEODME2000 (2)		
0.0049	0.9992	27.735	0.0169	0.9980	27.700	0.0500	0.9974	27.682
0.0148	0.9972	27.676	0.0308	0.9969	27.668	0.1048	0.9936	27.572
0.0289	0.9948	27.607	0.0458	0.9954	27.624	0.1318	0.9914	27.508
0.0396	0.9928	27.548	0.0603	0.9940	27.583	0.1487	0.9883	27.417
0.0498	0.9899	27.464	0.0895	0.9883	27.417	0.1782	0.9783	27.127
0.0587	0.9851	27.324	0.1204	0.9748	27.025	0.1937	0.9745	27.016
0.0693	0.9791	27.150	0.1386	0.9606	26.613	0.2288	0.9602	26.601
0.0796	0.9662	26.775						
0.0894	0.9439	26.129						
Acetonitrile (1) + PEO400 (2)			Acetonitrile (1) + PPO400 (2)					
0.0051	0.9992	27.735	0.0049	0.9993	27.738			
0.0100	0.9985	27.714	0.0101	0.9983	27.708			
0.0300	0.9963	27.65	0.0332	0.9958	27.636			
0.0597	0.9923	27.534	0.0600	0.9921	27.528			
0.0810	0.9875	27.394	0.0897	0.9848	27.316			
0.1094	0.9759	27.057	0.1209	0.9627	26.674			
0.1384	0.9319	25.782						

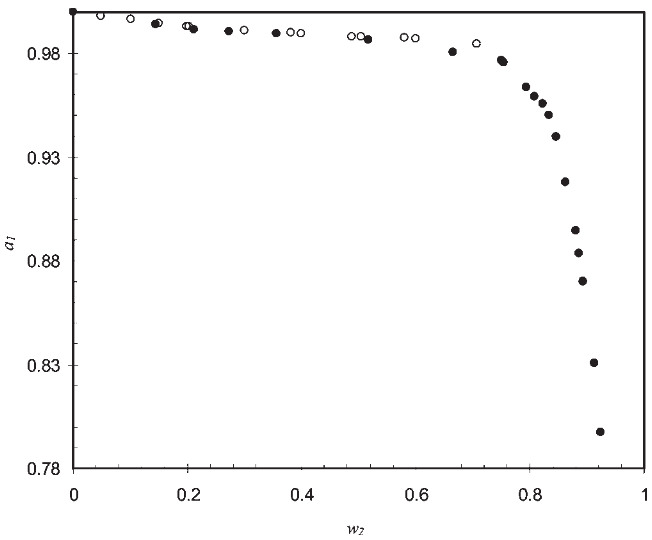

Figure 1. Comparison between the plot of water activity, a_1, against polymer mass fraction, w_2, for the water (1) + PPO400 (2) system at 318.15 K: ○, this work; ●, ref 23.

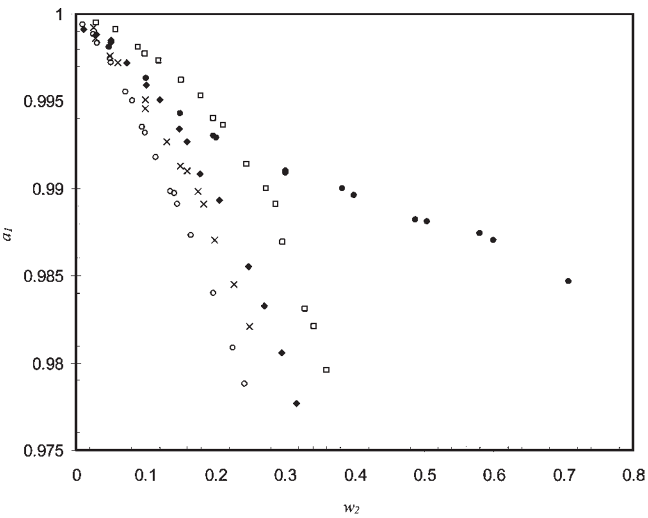

Figure 2. Variation of the water activity data, a_1, as a function of polymer mass fraction, w_2, for water (1) + polymer (2) systems at 318.15 K: ○, PEODME250; ♦, PEODME500; □, PEODME2000; ×, PEO400; ●, PPO400.

infinite dilution apparent specific isentropic compressibilities, κ_ϕ^0, for PVP in nonaqueous solutions decrease as temperature increases; however, these values in aqueous solutions increase by increasing temperature.[51] Increasing the temperature reduces the electrostriction; therefore, some water molecules are released into the bulk, thereby making the medium more compressible, and the values of κ_ϕ^0 become greater. However, in the case of nonaqueous polymer solutions, the interaction between polymer and nonaqueous solvents decreases by decreasing temperature; therefore, the medium becomes more compressible, and the values of κ_ϕ^0 increase as temperature decreases.

3.2. Theoretical Results. In this work, for the correlation of solvent activity for the investigated systems the segment-based local composition models NRTL[39] and Wilson[41] as well as the Flory−Huggins model[43] were considered. In the all of these models, the activity coefficient of the solvent (1) is considered as the sum of the combinatorial, $\ln \gamma_1^{\mathrm{Comb}}$, and the residual contribution, $\ln \gamma_1^{\mathrm{Res}}$:

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

For all of the models the Flory−Huggins expression was used for the combinatorial contribution, and the Flory−Huggins, NRTL, and Wilson models were used for the residual contribution.

Flory−Huggins Combinatorial Term. The Flory−Huggins equation for the combinatorial contribution of the activity coefficient

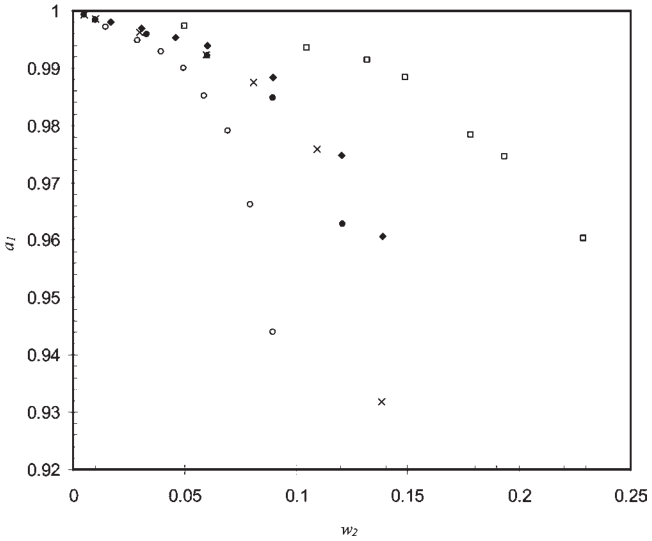

Figure 3. Variation of the acetronitrile activity data, a_1, as a function of polymer mass fraction, w_2, for acetronitrile (1) + polymer (2) systems at 318.15 K: ○, PEODME250; ◆, PEODME500; □, PEODME2000; ×, PEO400; ●, PPO400.

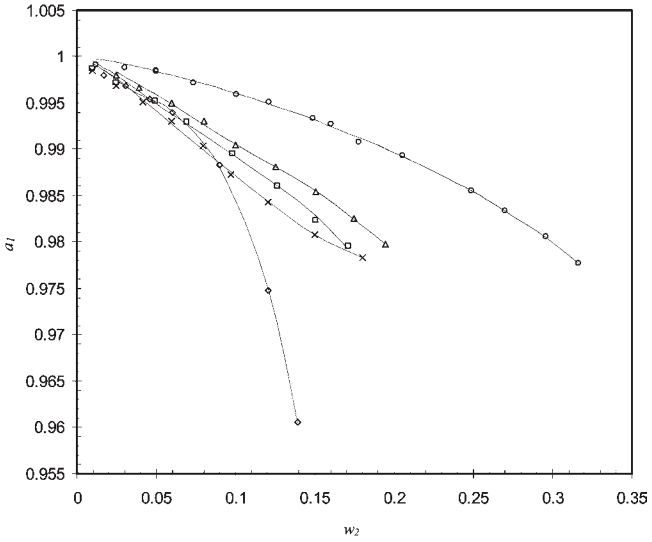

Figure 4. Variation of the solvent activity, a_1, as a function of polymer mass fraction, w_2, for solutions of PEODME500 in different solvents investigated in this work at $T = 318.15$ K: ○, water; △, methanol; □, ethanol; ×, 2-propanol; ◇, acetonitrile; —, calculated by Wilson model.

of the solvent can be written as:

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

where ϕ_i and x_i are the volume fraction and the mole fraction of the component i, respectively. r_i is the number of the segments in the component i. This equation accounts for the contribution for the excess entropy associated with random mixing. In this equation

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

where n_i is the number of moles of the component i.

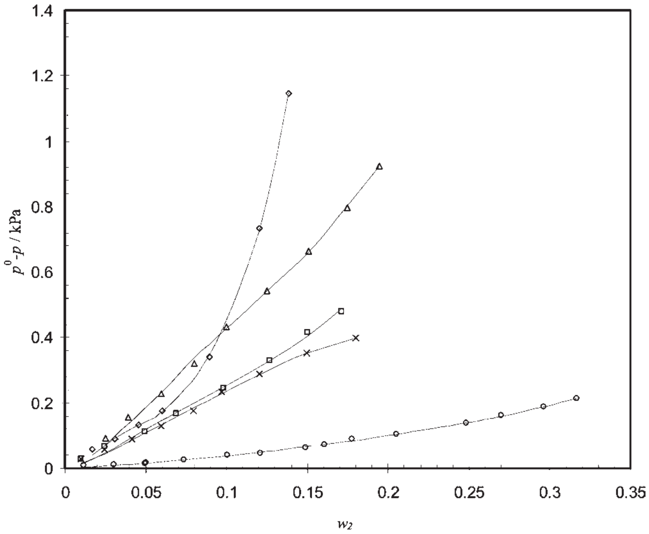

Figure 5. Variation of the vapor pressure depression, $p^\circ - p$, as a function of polymer mass fraction, w_2, for solutions of PEODME500 in different solvents investigated in this work at $T = 318.15$ K: ○, water; △, methanol; □, ethanol; ×, 2-propanol; ◇, acetonotrile; —, calculated by Wilson model.

Flory–Huggins Residual Term.

$$\ln \gamma_1^{\text{FH}} = \chi_{12}{\phi_2}^2 \tag{6}$$

where χ_{12} is the interaction parameter of the system.

NRTL Residual Term.

$$\frac{1}{r_1}\ln \gamma_1^{\text{NRTL}} = \phi_2^2 \left(\frac{a_{21}}{RT} \exp \frac{\left(-\alpha \frac{a_{21}}{RT}\right)^2}{\left(\phi_1 + \phi_2 \exp\left(-\alpha \frac{a_{21}}{RT}\right)\right)^2} + \frac{a_{12}}{RT} \exp \frac{\left(-\alpha \frac{a_{12}}{RT}\right)}{\left(\phi_2 + \phi_1 \exp\left(-\alpha \frac{a_{12}}{RT}\right)\right)^2} \right) \tag{7}$$

where α is the nonrandomness factor and the NRTL parameters a_{ij} are fitted to the experimental data.

Wilson Residual Term.

$$-\frac{1}{Cr_1}\ln \gamma_1^{\text{Wilson}} = \ln\left(\phi_1 + \phi_2 \exp\left(-\frac{E_{21}}{CRT}\right)\right) + \phi_1\left(1 - \frac{\left(\phi_1 + \phi_2 \exp\left(-\frac{E_{21}}{CRT}\right)\right)}{\phi_1 + \phi_2 \exp\left(-\frac{E_{21}}{CRT}\right)}\right) + \phi_2\left(\exp\left(-\frac{E_{12}}{CRT}\right) - \frac{\left(\phi_2 + \phi_1 \exp\left(-\frac{E_{12}}{CRT}\right)\right)}{\phi_2 + \phi_1 \exp\left(-\frac{E_{12}}{CRT}\right)}\right) \tag{8}$$

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

Table 6. Parameters of the NRTL, Wilson, and Flory−Huggins Equations along with the Corresponding Relative Percentage Deviations (Dev %)

	NRTL			Wilson			Flory−Huggins	
system	$a_{12} \cdot 10^{-3}$	$a_{21} \cdot 10^{-3}$	Dev %	$E_{12} \cdot 10^{-3}$	$E_{21} \cdot 10^{-3}$	Dev %	χ_{12}	Dev %
water (1) + PEODME250 (2)	0.912	0.347	0.10	2.095	−0.855	0.11	0.531	0.04
water (1) + PEODME500 (2)	0.912	0.347	0.06	2.095	−0.855	0.08	0.503	0.03
water (1) + PEODME2000 (2)	0.912	0.347	0.12	2.095	−0.855	0.09	0.462	0.07
water (1) + PEO400 (2)	0.105	1.383	0.02	−0.459	1.772	0.02	0.462	0.02
water (1) + PPO400(2)	−0.529	4.105	0.02	−7.809	1.268	0.02	0.777	0.59
methanol (1) + PEODME250 (2)	−1.362	10.873	0.04	−16.952	40.710	0.03	0.090	0.04
methanol (1) + PEODME500 (2)	−1.362	10.873	0.05	−16.952	40.710	0.06	0.205	0.05
methanol (1) + PEODME2000 (2)	−1.362	10.873	0.10	−16.952	40.710	0.09	0.197	0.14
methanol (1) + PEO400 (2)	−1.677	11.298	0.04	−18.708	135.6	0.04	0.023	0.05
methanol (1) + PPO400(2)	−1.325	10.765	0.04	−18.095	135.6	0.03	0.165	0.05
ethanol (1) + PEODME250 (2)	6.533	−4.454	0.05	19.845	−14.964	0.05	0.529	0.04
ethanol (1) + PEODME500 (2)	6.533	−4.454	0.05	19.845	−14.964	0.05	0.298	0.02
ethanol (1) + PEO400 (2)	0.021	0.712	0.03	0.492	0.156	0.03	0.247	0.03
ethanol (1) + PPO400(2)	7.551	−5.134	0.03	8.296	−6.879	0.05	0.243	0.05
acetonitrile (1) + PEODME250 (2)	22.722	−12.698	0.25	66.130	−39.115	0.24	−5.769	0.51
acetonitrile (1) + PEODME500 (2)	15.057	−9.252	0.11	43.822	−28.752	0.11	−1.631	0.25
acetonitrile (1) + PEODME2000 (2)	−5.866	3.844	0.18	−11.541	11.541	0.19	−0.666	0.20
acetonitrile (1) + PEO400 (2)	19.889	−11.216	0.31	57.795	−34.940	0.31	−3.762	0.63
acetonitrile (1) + PPO400(2)	15.897	−9.637	0.11	46.264	−29.935	0.11	−1.775	0.24
2-propanol (1) + PEODME250 (2)	6.085	−3.944	0.08	18.735	−13.951	0.08	0.952	0.02
2-propanol (1) + PEODME500 (2)	6.085	−3.9444	0.09	18.735	−13.951	0.09	0.537	0.05
2-propanol (1) + PEO400 (2)	0.328	1.240	0.02	2.691	−1.394	0.02	0.507	0.02
2-propanol (1) + PPO400(2)	2.645	−1.743	0.02	8.382	−6.806	0.02	0.329	0.02

A value of $r = 1$ was used for solvents, and for polymers 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 PEODME250, PEODME500, PEODME2000, PEO400, and PPO400 at 298.15 K are (0.9662,[52] 0.9328,[52] 0.8344,[52] 0.8904,[53] and 0.9962[54]) $cm^3 \cdot g^{-1}$, respectively. The values of the nonrandomness factor α and the effective coordination number C were set to 0.25[55] and 10,[56] respectively. The segment-based local composition models, NRTL and Wilson, as well as the Flory−Huggins model were used for the correlation of the experimental solvent activity data, and the obtained parameters for the studied systems are presented in Table 6 along with the corresponding relative percentage deviations (Dev %) of the fit. On the basis of the deviations, we conclude that all of the investigated models represent the experimental solvent activity data of polymer solutions, with good accuracy. As can be seen from Table 6, except for the acetonitrile + polymer systems, the obtained parameters of the segment-based local composition models, NRTL and Wilson, are independent of polymer molar mass.

4. CONCLUSIONS

The VPO method was used for the determination of the solvent activities of solutions of PEODME250, PEODME500, PEODME2000, PEO400, and PPO400 in water, methanol, ethanol, 2-propanol, and acetonitrile at 318.15 K in the semidiluted polymer concentration range, and the results were successfully correlated by the NRTL, Wilson, and Flory−Huggins models. It was found that the activity of a volatile solvent at a given mass concentration of homologous polymers is inversely proportional to the molar mass of the polymer. Furthermore, because of the greater proportion of hydrocarbon in the PPO molecule, the water activity of the concentrated aqueous PPO solutions ($0.23 < w_2$) is very larger than those of the other investigated polymer + water solutions. Regarding the effect of the type of solvent, the results show that the solvent activity of the investigated polymer solutions for polymer mass fraction smaller and higher than about 0.09 respectively follow the order 2-propanol < acetonitrile ≈ ethanol < methanol < water and acetonitrile < 2-propanol < ethanol < methanol < water.

■ AUTHOR INFORMATION

Corresponding Author

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

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