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Effect of Temperature and Solvent Composition on the Intrinsic Viscosity of Poly(ethylene glycol)/Poly(vinyl pyrrolidone) Blends in Water−Ethanol Solutions

Abbas Mehrdad,* Islam Talebi, and Mohammad Reza Rostami

Department of Physical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

ABSTRACT: In this work, the intrinsic viscosities of poly(ethylene glycol)/poly(vinyl pyrrolidone) (PEG/PVP) blends were measured in water−ethanol solutions from (283.1 to 313.1) K. The expansion factors of the polymer chains were calculated from the intrinsic viscosity data. The thermodynamic parameters (entropy of dilution parameter, the heat of dilution parameter, theta temperature, polymer−solvent interaction parameter, and second osmotic virial coefficient) were derived by the temperature dependence of the polymer chain expansion factor. The thermodynamic parameters indicate that mixed water−ethanol are changed to the weak solvents for PEG/PVP blends by increasing temperature. The compatibility of PEG/PVP blends was explained in terms of the difference between experimental and ideal values of the Huggins parameter, solvent−polymer interaction parameter, and second osmotic virial coefficient. The results indicate that the PEG/PVP blends are compatible in mixed water−ethanol.

INTRODUCTION

The blending of polymers is one of the simplest means to obtain a variety of physical and chemical properties from the constituent polymers.[1] The widespread potential applications for polymer blends have led in recent years to an increasing research effort on miscibility as well as on the phase separation process.[2] A simple method to analyze polymer−polymer miscibility in solution is the viscometric technique.[3] The viscosity study on ternary system of two different polymers and a solvent has been a subject of continuing interest, mainly due to its simplicity and importance in the characterization of the intermolecular interaction between the two different polymers in solution.[4] The rheology of polymer solutions is significantly affected by the quality of the solvent, mainly because polymer−solvent interactions play a crucial role in the conformation of the polymer chain in solution.[5] The conformation of the polymer chain in solution can be affected the thermodynamic parameters (such as polymer−solvent interaction parameter) and hydrodynamic parameters (such as expansion factor and intrinsic viscosity); therefore, the compatibility of polymer can be explained in terms of the thermodynamic and hydrodynamic parameters. Previous findings indicate that the poly(ethylene glycol)/poly(vinyl pyrrolidone) (PEG/PVP) blends in water were incompatible due to repulsive interactions between the polymers.[6−8] The aim of this study was to find the some thermodynamic and hydrodynamic parameters of PEG/PVP blends in mixed water−ethanol solutions and to explain the compatibility in terms of the thermodynamic parameters.

THEORETICAL SECTION

In a good solvent the polymer molecule expands. The expansion factor, α, which describes the excluded volume effect, is given by:[9]

$$\alpha = \left(\frac{\langle R^2\rangle}{\langle R^2\rangle_0}\right)^{0.5} \qquad (1)$$

where $\langle R^2\rangle$ and $\langle R^2\rangle_0$ are the mean square end-to-end distance of a polymer chain in expanded and in unperturbed chains, respectively. Flory and Fox suggested that the relation of expansion factor with intrinsic viscosity, $[\eta]$, is given by:[10]

$$\alpha^3 = \frac{[\eta]M}{\Phi\langle R^2\rangle_0^{\ 1.5}} \qquad (2)$$

where Φ and M are the Flory constant and molecular weight of polymer. The Flory constant is equal $2.8\cdot10^{20}$.

In the random flight chains model with restricted bond angles φ but rotations about the bonds which are not restricted, $\langle R^2\rangle_0$ is given by:[11]

$$\langle R^2\rangle_0 = Nl^2\frac{1-\cos\varphi}{1+\cos\varphi} + 2l^2\cos\varphi\frac{1+(\cos\varphi)^N}{(1+\cos\varphi)^2} \qquad (3)$$

where N and l are the number of bonds existing in the polymer chain and the bond length, respectively. However, in the case PEG and PVP φ = 109.5°. The value of l in the case of PEG is derived by taking the average from the bond length for (C−C) and (C−O), and the value of l in the case of PVP is the equal bond length of (C−C). The used bond lengths are l_{C-C} = 0.153 and l_{C-O} = 0.143 nm.[12]

Mehrdad et al.[8] have proposed that the expansion factor in the polymer blends can be put in the form:

$$\alpha_m^3 = \frac{[\eta]M}{\Phi(\langle R^2\rangle_{0A}^{0.5}w_A + \langle R^2\rangle_{0B}^{0.5}w_B)^3} \qquad (4)$$

where the subscript m denotes the mixture. $w_A = C_A/(C_A + C_B)$ and $w_B = C_B/(C_A + C_B)$ are the weight fractions of polymers A and B in the polymer blends, respectively. C_A and C_B are the concentrations of polymer A and B, respectively.

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Table 1. Viscosities, η, of Three PEG/PVP Blends in Mixed Water−Ethanol ($\varphi_E = 0.05$) at Different Temperatures

C/kg·m^{-3}	$10^3\,\eta \pm 4\cdot10^{-3}$/kg·m^{-1}·s^{-1}						
	T/K = 283.1	T/K = 288.1	T/K = 293.1	T/K = 298.1	T/K = 303.1	T/K = 308.1	T/K = 313.1
				$W_{PEG} = 0.75$			
0.00	1.605	1.377	1.198	1.052	0.931	0.831	0.748
4.00	1.861	1.591	1.378	1.204	1.063	0.945	0.847
4.97	1.928	1.647	1.425	1.244	1.098	0.974	0.872
5.98	1.996	1.703	1.473	1.285	1.132	1.005	0.899
6.93	2.061	1.760	1.521	1.326	1.167	1.035	0.925
8.00	2.142	1.825	1.575	1.372	1.207	1.069	0.955
8.95	2.210	1.883	1.624	1.415	1.243	1.100	0.982
9.96	2.284	1.945	1.676	1.458	1.281	1.133	1.011
10.96	2.362	2.010	1.732	1.506	1.321	1.168	1.040
11.96	2.440	2.075	1.786	1.553	1.362	1.203	1.070
12.92	2.515	2.139	1.841	1.600	1.401	1.238	1.101
				$W_{PEG} = 0.50$			
3.98	1.830	1.566	1.357	1.188	1.048	0.932	0.836
4.97	1.888	1.615	1.399	1.223	1.078	0.959	0.859
5.97	1.949	1.665	1.441	1.258	1.109	0.986	0.882
6.95	2.009	1.715	1.483	1.295	1.140	1.012	0.905
7.94	2.070	1.766	1.525	1.330	1.171	1.039	0.929
8.93	2.133	1.818	1.570	1.369	1.204	1.067	0.953
9.90	2.195	1.870	1.614	1.405	1.235	1.093	0.977
10.92	2.262	1.925	1.661	1.446	1.270	1.123	1.002
11.89	2.327	1.978	1.706	1.483	1.302	1.151	1.026
12.91	2.395	2.035	1.754	1.524	1.337	1.181	1.053
				$W_{PEG} = 0.25$			
3.98	1.798	1.539	1.334	1.168	1.032	0.917	0.823
4.99	1.849	1.582	1.370	1.199	1.058	0.941	0.843
5.95	1.899	1.624	1.405	1.229	1.084	0.962	0.863
7.94	2.006	1.714	1.480	1.292	1.139	1.010	0.904
9.95	2.116	1.806	1.559	1.359	1.196	1.059	0.947
11.90	2.227	1.898	1.637	1.425	1.254	1.109	0.990
13.91	2.345	1.998	1.722	1.497	1.315	1.163	1.036
15.93	2.471	2.102	1.809	1.573	1.378	1.217	1.083
17.93	2.597	2.206	1.897	1.647	1.443	1.273	1.133
19.87	2.721	2.310	1.987	1.723	1.508	1.330	1.183

Flory and Fox further suggested that the temperature dependence of the expansion factor is as follows:[10]

$$\alpha^5 - \alpha^3 = \left(\frac{27}{2^{1.5}\pi^{1.5}}\right)\left(\frac{\bar{\nu}^2}{N_A V_s}\right)\left(\frac{\langle R^2\rangle_0}{M}\right)^{-1.5}\Psi M^{0.5}\left(1 - \frac{\theta}{T}\right) \quad (5)$$

where V_s, $\bar{\nu}$, N_A, Ψ, θ, and T are the molar volume of solvent, the partial specific volume of the polymer, Avogadro's number, the entropy of dilution parameter, theta temperature, and absolute temperature, respectively. On the other hand, the heat of dilution parameter, κ, is given by:[13]

$$\kappa = \frac{\theta\Psi}{T} \quad (6)$$

The polymer−solvent interaction parameter, χ, can be expressed in terms of entropy and heat of dilution parameter as:[13]

$$\chi = 0.5 + \kappa - \Psi \quad (7)$$

From the entropy of dilution parameter and the heat of dilution parameter, the second osmotic virial coefficient, A, can be calculated. The second osmotic virial coefficient in terms of the entropy of dilution parameter and the heat of dilution parameter can be expressed:[13]

$$A = \frac{\bar{\nu}^2}{V_s}(\Psi - \kappa)F(\alpha) \quad (8)$$

where

$$F(\alpha) = \sum_{n=0}^{\infty}\frac{(-2(\alpha^2 - 1))^n}{(n+1)!(n+1)^{1.5}} \quad (9)$$

In the method of dilution viscosity solution for evaluating compatibility of polymers, the measurements were carried out in solutions of A/B blends at constant weight ratio of polymer A to B. In this method the compatibility is estimated by comparison of the experimental and ideal values of interaction parameter.[14] In the solutions of polymer blends, the relation of reduced viscosity, $(\eta_{red})_m$, versus C_m is given by:[3]

$$(\eta_{red})_m = [\eta]_m + b_m C_m \quad (10)$$

where $b_m = k_H[\eta]_m{}^2$ and k_H is Huggins constant.

The experimental value of the interaction parameter, b_m^{exp}, is determined from the slope of plot of reduced viscosity, $(\eta_{red})_m$, versus C_m.

Garcia et al.[3] defined the ideal value of interaction parameter by the expression:

$$b_m^{id} = b_A w_A{}^2 + b_B w_B{}^2 \quad (11)$$

where b_A and b_B are the interaction parameters for polymers A and B in binary systems. The polymer blend is compatible if $b_m^{exp} - b_m^{id} > 0$ and is incompatible if $b_m^{exp} - b_m^{id} < 0$.

Table 2. Viscosities, η, of Three PEG/PVP Blends in Mixed Water−Ethanol (φ_E = 0.10) at Different Temperatures

C/kg·m^{-3}	$10^3\,\eta \pm 4\cdot10^{-3}$/kg·m^{-1}·s^{-1}						
	T/K = 283.1	T/K = 288.1	T/K = 293.1	T/K = 298.1	T/K = 303.1	T/K = 308.1	T/K = 313.1
				W_{PEG} = 0.75			
0.00	1.948	1.644	1.409	1.224	1.073	0.950	0.847
2.01	2.092	1.764	1.510	1.310	1.147	1.014	0.903
3.00	2.167	1.826	1.562	1.355	1.185	1.047	0.931
4.00	2.244	1.890	1.617	1.401	1.224	1.080	0.960
4.95	2.319	1.953	1.670	1.446	1.261	1.113	0.988
5.97	2.403	2.024	1.729	1.495	1.304	1.150	1.020
6.89	2.482	2.089	1.784	1.542	1.344	1.183	1.049
7.91	2.570	2.164	1.846	1.595	1.387	1.222	1.082
8.89	2.660	2.237	1.907	1.645	1.431	1.259	1.114
9.91	2.750	2.316	1.972	1.698	1.477	1.298	1.148
				W_{PEG} = 0.50			
0.99	2.012	1.697	1.454	1.262	1.105	0.978	0.871
1.98	2.078	1.752	1.500	1.300	1.138	1.007	0.896
2.97	2.145	1.808	1.548	1.341	1.172	1.036	0.922
3.96	2.213	1.866	1.595	1.382	1.207	1.065	0.948
4.95	2.283	1.924	1.645	1.421	1.242	1.096	0.975
5.93	2.356	1.984	1.695	1.465	1.278	1.128	1.002
6.92	2.427	2.043	1.746	1.506	1.315	1.159	1.029
7.91	2.507	2.109	1.800	1.554	1.354	1.193	1.058
8.87	2.581	2.173	1.852	1.597	1.392	1.225	1.085
9.89	2.659	2.236	1.907	1.643	1.430	1.260	1.115
				W_{PEG} = 0.25			
0.99	2.003	1.690	1.447	1.256	1.100	0.974	0.868
1.98	2.060	1.737	1.486	1.290	1.129	0.998	0.889
2.97	2.118	1.785	1.527	1.323	1.158	1.023	0.911
3.96	2.177	1.835	1.568	1.359	1.188	1.050	0.934
4.95	2.237	1.886	1.610	1.393	1.218	1.075	0.956
5.93	2.298	1.938	1.653	1.431	1.249	1.102	0.981
6.92	2.361	1.992	1.697	1.468	1.281	1.129	1.005
7.91	2.431	2.049	1.746	1.509	1.318	1.160	1.030
8.88	2.497	2.104	1.792	1.550	1.350	1.187	1.053
9.89	2.565	2.163	1.841	1.590	1.386	1.218	1.080

Mehrdad et al.[8] have proposed another compatibility criterion which is based on the difference between experimental and ideal values of the polymer−solvent interaction parameter. On the basis of this criterion, the polymer blend is compatible if $\Delta\chi = \chi_m^{exp} - \chi_m^{id} > 0$ and is incompatible if $\Delta\chi = \chi_m^{exp} - \chi_m^{id} < 0$, whereas χ_m^{id} is defined by:

$$\chi_m^{id} = \chi_A w_A + \chi_B w_B \qquad (12)$$

where χ_A and χ_B are the polymer−solvent interaction parameters for polymers A and B in binary systems.

The compatibility of polymers is a result of interaction of polymer−polymer and polymer−solvent. Interactions of polymers can be affected the second osmotic virial coefficient; therefore we define the new compatibility criterion based on the difference between experimental and ideal values of the second osmotic virial coefficient. When two polymers are compatible, this means that the interactions of segments of polymer A with segments of polymer B are favored toward the interactions of segments of each polymer with solvent. When the interactions of segments of polymer A with segments of polymer B are favored toward the interactions of segments of each polymer with solvent, the quality of solvent is weak, and in weak solvent the second osmotic virial coefficient has a low value; therefore the polymer blend is compatible if $\Delta A = A_m^{exp} - A_m^{id} < 0$ and is incompatible if $\Delta A = A_m^{exp} - A_m^{id} > 0$, whereas A_m^{id} is defined by:

$$A_m^{id} = A_A w_A + A_B w_B \qquad (13)$$

where A_A and A_B are the second osmotic virial coefficients for polymers A and B in binary systems.

EXPERIMENTAL SECTION

Materials. The poly(ethylene glycol) (PEG) used in this study was purchased from Merck Chemical Co. and had a reported nominal average molar mass of 20 kg·mol^{-1}. The poly(vinyl pyrrolidone) (PVP) used in this study was purchased from Fluka Chemical Co. and had a reported nominal average molar mass of 58 kg·mol^{-1}. Ethanol was purchased from Merck Chemical Co. and had a reported mass fraction purity of 0.995. PEG, poly(vinyl pyrrolidone), and ethanol were used without further purification. Distilled water was used for the preparation of solutions.

Apparatus and Procedure. Gel permeation chromatography (GPC), which was kindly performed by Jahad-e-Keshavarzi Engineering Research Center, gave an average molar mass of (21.1 and 56.3) kg·mol^{-1} with a polydispersity index of 1.20 and 1.25 for PEG and PVP, respectively. PEG/PVP blend solutions with a weight ratio (w_{PEG} = 0.75, 0.50, and 0.25) were prepared gravimetrically by an analytical balance (Sartorius CP224 S) with an uncertainty of $\pm\,2\cdot10^{-7}$ kg and were dispersed into preprepared ethanol aqueous solutions with volume fractions of ethanol φ_E = 0.05, 0.10, and 0.15. The uncertainties of the ethanol volume fractions and concentration of polymer solutions are ± 0.2 % and $\pm\,5\cdot10^{-3}$ kg·m^{-3}, respectively. The polymer solutions were filtered before use by a filter with an aperture of 75 μm, and their

Table 3. Viscosities, η, of Three PEG/PVP Blends in Mixed Water−Ethanol ($\varphi_E = 0.15$) at Different Temperatures

$C/\text{kg}\cdot\text{m}^{-3}$	$10^3\ \eta \pm 6\cdot10^{-3}/\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$						
	$T/\text{K} = 283.1$	$T/\text{K} = 288.1$	$T/\text{K} = 293.1$	$T/\text{K} = 298.1$	$T/\text{K} = 303.1$	$T/\text{K} = 308.1$	$T/\text{K} = 313.1$
$W_{PEG} = 0.75$							
0.00	2.362	1.970	1.668	1.432	1.242	1.089	0.964
3.96	2.723	2.266	1.913	1.636	1.415	1.236	1.091
5.89	2.912	2.419	2.042	1.744	1.506	1.314	1.159
7.88	3.107	2.581	2.175	1.856	1.601	1.395	1.230
9.85	3.315	2.750	2.316	1.972	1.704	1.484	1.304
11.83	3.531	2.928	2.465	2.103	1.811	1.575	1.383
13.73	3.752	3.108	2.613	2.226	1.915	1.664	1.459
15.76	3.985	3.302	2.777	2.363	2.031	1.763	1.544
17.70	4.227	3.497	2.936	2.497	2.144	1.860	1.629
19.20	4.398	3.641	3.058	2.602	2.233	1.936	1.694
$W_{PEG} = 0.50$							
3.93	2.679	2.229	1.885	1.613	1.395	1.219	1.077
5.87	2.845	2.366	1.999	1.709	1.477	1.289	1.136
7.84	3.023	2.511	2.118	1.810	1.561	1.362	1.201
9.83	3.201	2.661	2.243	1.916	1.652	1.440	1.267
11.77	3.393	2.815	2.371	2.020	1.747	1.515	1.333
13.73	3.588	2.973	2.504	2.133	1.836	1.598	1.403
15.69	3.799	3.147	2.646	2.252	1.940	1.687	1.480
17.67	4.011	3.319	2.790	2.372	2.039	1.776	1.552
19.65	4.234	3.503	2.940	2.498	2.146	1.867	1.635
$W_{PEG} = 0.25$							
5.91	2.790	2.319	1.957	1.674	1.447	1.264	1.116
6.88	2.867	2.383	2.011	1.717	1.483	1.295	1.143
7.88	2.945	2.447	2.062	1.761	1.521	1.327	1.171
8.85	3.022	2.509	2.115	1.808	1.561	1.361	1.199
9.81	3.105	2.579	2.174	1.855	1.600	1.395	1.228
10.82	3.186	2.647	2.229	1.902	1.640	1.430	1.258
11.77	3.268	2.711	2.285	1.948	1.681	1.463	1.287
13.75	3.448	2.857	2.403	2.048	1.763	1.534	1.349
15.73	3.624	3.003	2.526	2.151	1.852	1.610	1.414
17.68	3.810	3.155	2.648	2.254	1.938	1.686	1.478
19.68	4.001	3.310	2.786	2.365	2.030	1.766	1.547

viscosities were measured using a jacketed Ubbelohde viscometer with a 0.4 mm capillary. The temperature of solutions was kept constant by a temperature controller (Eyela, UA-10, Tokyo Rikakiai Co.) with an uncertainty of ± 0.1 K. The flow times for solutions which used in this work were never less than 193 s. The flow times were determined from an average of three readings with the uncertainty of ± 0.2 s. The absolute viscosity values were calculated by the following equation:

$$\eta = Ldt - \frac{Nd}{t^2} \tag{14}$$

where η is the absolute viscosity of the solution, t is the flow time, d is the density of the solution, and L and N are constants characteristic of the viscometer. Densities were measured with a U-tube vibrating densimeter (Kyoto Electronic DA-210) with an uncertainty of $\pm\ 3\cdot10^{-2}\ \text{kg}\cdot\text{m}^{-3}$.

RESULTS AND DISCUSSION

The flow times of solutions of PEG/PVP blends with a weight ratio (w_{PEG} = 0.75, 0.50, and 0.25) in mixed water−ethanol with volume fractions of ethanol of φ_E = 0.05, 0.10, and 0.15 were measured at various temperatures and concentrations of polymer, and from these data, viscosities, η, are calculated. The calculated viscosities in various conditions are listed in Tables 1 to 3. According to the eq 10, the plot of reduced viscosity versus concentration gives a straight line which slope and intercept are interaction parameter, b_m^{exp}, and intrinsic viscosity, $[\eta]_m^{exp}$, respectively. The obtained interaction parameters are listed in Table 4. The obtained intrinsic viscosities and Huggins constants are listed in Table 5. For flexible polymer molecules the Huggins constant is expected to be about 0.35 in good solvents but higher in poor solvents.[15] A comparison of the results of Table 3 with our previous data reveals that the Huggins constant for PEG/PVP blends in mixed water−ethanol are slightly higher than those in pure water.[8] It seems likely that the high values for Huggins constants arise from the aggregation of polymer molecules. The obtained intrinsic viscosities of PEG/PVP blends in mixed water−ethanol are decreased by increasing temperature. In the weak solvent polymer−polymer interactions are favored to polymer−solvent interactions, and it causes a reduction in polymer coil's hydrodynamic volume and intrinsic viscosity. Therefore, the mixed water−ethanol solutions were changed to the weak solvents for PEG/PVP blends by increasing temperature. Similar results were found for PEG/PVP blends in water[8] and for PEG[16] and PVP[17] in mixed water−ethanol solutions. The values of expansion factor were calculated using the data of Table 5 and eq 4. The calculated expansion factors of PEG/PVP blends at different temperatures and various volume fractions of ethanol are listed in Table 6. The data of Table 6 indicate that the values of expansion factor were decreased by increasing temperature; therefore, the chain of PEG and PVP shrinks and the end-to-end distance become smaller by increasing temperature. This behavior may be due to the effect of temperature on the interactions of segment−segment and segment−solvent.

Table 4. Experimental and Ideal Interaction Parameter, b, of PEG/PVP Blends in Different Solvent Compositions at Different Temperatures

T/K	$10^4\ b_m^{exp} \pm 8\cdot10^{-2}/m^6\cdot kg^{-2}$				$10^4\ b_m^{id} \pm 8\cdot10^{-2}/m^6\cdot kg^{-2}$		
	$W_{PEG} = 0.75$	$W_{PEG} = 0.50$	$W_{PEG} = 0.25$		$W_{PEG} = 0.75$	$W_{PEG} = 0.50$	$W_{PEG} = 0.25$
				$\varphi_E = 0.05$			
283.1	4.47	3.28	3.04		3.40	2.12	1.90
288.1	4.41	2.82	2.86		3.16	1.97	1.76
293.1	4.35	2.86	2.93		3.07	1.89	1.64
298.1	4.58	2.61	2.77		2.89	1.78	1.54
303.1	3.99	2.51	2.53		2.76	1.70	1.49
308.1	4.00	2.14	2.59		2.62	1.63	1.44
313.1	3.81	2.19	2.49		2.49	1.54	1.35
				$\varphi_E = 0.10$			
283.1	6.11	4.26	3.88		3.27	2.09	1.96
288.1	6.31	4.22	4.35		3.22	2.04	1.87
293.1	5.95	3.95	4.23		3.11	1.92	1.70
298.1	5.24	3.93	4.11		2.95	1.89	1.77
303.1	4.71	3.96	4.06		2.86	1.86	1.79
308.1	4.47	3.63	3.73		2.65	1.72	1.66
313.1	3.98	3.38	3.48		2.55	1.67	1.64
				$\varphi_E = 0.15$			
283.1	4.29	4.01	3.40		3.37	2.13	1.96
288.1	4.30	3.87	3.33		3.42	2.14	1.94
293.1	4.22	3.69	3.24		3.31	2.10	1.94
298.1	4.38	3.57	3.31		3.25	2.08	1.96
303.1	4.23	3.54	3.24		3.21	2.07	1.97
308.1	4.19	3.73	3.24		3.13	2.02	1.91
313.1	3.91	3.52	2.99		2.97	1.92	1.83

Table 5. Intrinsic Viscosities, $[\eta]_m$, and Huggins Constant, k_H, of PEG/PVP Blends in Different Solvent Compositions at Different Temperatures

T/K	$[\eta]_m \pm 7\cdot10^{-5}/m^3\cdot kg^{-1}$				$k_H \pm 8\cdot10^{-3}$		
	$W_{PEG} = 0.75$	$W_{PEG} = 0.50$	$W_{PEG} = 0.25$		$W_{PEG} = 0.75$	$W_{PEG} = 0.50$	$W_{PEG} = 0.25$
				$\varphi_E = 0.05$			
283.1	0.03811	0.03390	0.02899		0.308	0.285	0.362
288.1	0.03710	0.03336	0.02845		0.320	0.253	0.353
293.1	0.03585	0.03224	0.02733		0.338	0.275	0.392
298.1	0.03436	0.03136	0.02659		0.388	0.265	0.392
303.1	0.03387	0.03054	0.02614		0.348	0.269	0.370
308.1	0.03263	0.02984	0.02505		0.376	0.240	0.413
313.1	0.03151	0.02871	0.02425		0.384	0.266	0.423
				$\varphi_E = 0.10$			
283.1	0.03555	0.03276	0.02816		0.483	0.397	0.489
288.1	0.03496	0.03235	0.02763		0.516	0.403	0.570
293.1	0.03448	0.03189	0.02679		0.500	0.388	0.589
298.1	0.03403	0.03080	0.02614		0.452	0.414	0.601
303.1	0.03330	0.02988	0.02542		0.425	0.444	0.628
308.1	0.03257	0.02937	0.02483		0.421	0.421	0.605
313.1	0.03187	0.02875	0.02444		0.392	0.409	0.583
				$\varphi_E = 0.15$			
283.1	0.03683	0.03241	0.02866		0.316	0.382	0.414
288.1	0.03606	0.03192	0.02812		0.331	0.380	0.421
293.1	0.03541	0.03153	0.02757		0.337	0.371	0.426
298.1	0.03426	0.03083	0.02671		0.373	0.376	0.464
303.1	0.03357	0.03013	0.02609		0.375	0.390	0.476
308.1	0.03260	0.02904	0.02533		0.394	0.442	0.505
313.1	0.03201	0.02845	0.02494		0.382	0.435	0.481

Perhaps the interactions of segment—segment are favored toward segment—solvent by increasing temperature; therefore, the hydrodynamic volumes of the polymer coils become smaller by increasing temperature. For evaluating the theta temperature and entropy of dilution parameter, the values of $(\alpha^5 - \alpha^3)$ are plotted versus $1/T$. The plots of $(\alpha^5 - \alpha^3)$ versus $1/T$ are presented in Figure 1. From the intercept and slope of these plots the values of theta temperature and entropy of dilution parameter were calculated. The obtained

Table 6. Expansion Factor, α_m, of PEG/PVP Blends in Different Solvent Composition at Different Temperatures

T/K	$\alpha_m \pm 7\cdot10^{-3}$		
	$W_{PEG} = 0.75$	$W_{PEG} = 0.50$	$W_{PEG} = 0.25$
		$\varphi_E = 0.05$	
283.1	2.144	2.313	2.415
288.1	2.125	2.301	2.399
293.1	2.101	2.275	2.368
298.1	2.071	2.254	2.346
303.1	2.061	2.234	2.333
308.1	2.036	2.217	2.300
313.1	2.012	2.189	2.275
		$\varphi_E = 0.10$	
283.1	2.095	2.287	2.391
288.1	2.083	2.277	2.376
293.1	2.074	2.267	2.352
298.1	2.065	2.240	2.333
303.1	2.050	2.218	2.311
308.1	2.035	2.205	2.293
313.1	2.020	2.190	2.281
		$\varphi_E = 0.15$	
283.1	2.120	2.279	2.405
288.1	2.105	2.267	2.390
293.1	2.092	2.258	2.374
298.1	2.069	2.241	2.349
303.1	2.055	2.224	2.331
308.1	2.035	2.197	2.308
313.1	2.023	2.182	2.296

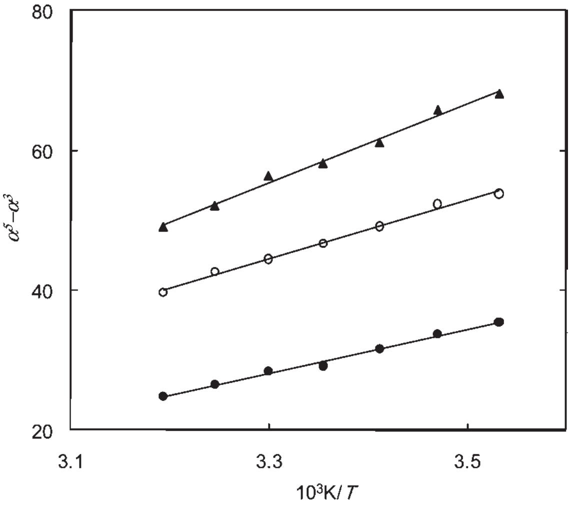

Figure 1. Plots of ($\alpha^5 - \alpha^3$) versus $1/T$ for blends of PEG/PVP in mixed water−ethanol ($\varphi_E = 0.05$); ●, $w_{PEG} = 0.75$; ○, $w_{PEG} = 0.50$; ▲, $w_{PEG} = 0.25$.

Table 7. Theta Temperature, θ, and Entropy of Dilution Parameter, Ψ, of PEG/PVP Blends in Different Solvent Compositions

W_{PEG}	$\varphi_E = 0.05$	$\varphi_E = 0.10$	$\varphi_E = 0.15$
		$\theta \pm 5$ K	
0.75	417	598	475
0.50	447	494	510
0.25	433	475	482
		$\Psi \pm 5\cdot10^{-3}$	
0.75	−0.351	−0.142	−0.267
0.50	−0.241	−0.191	−0.187
0.25	−0.205	−0.163	−0.176

Table 8. Heat of Dilution Parameter, κ, of PEG/PVP Blends in Different Solvent Compositions at Different Temperatures

T/K	$\kappa \pm 5\cdot10^{-3}$		
	$W_{PEG} = 0.75$	$W_{PEG} = 0.50$	$W_{PEG} = 0.25$
		$\varphi_E = 0.05$	
283.1	−0.517	−0.381	−0.314
288.1	−0.508	−0.374	−0.309
293.1	−0.499	−0.368	−0.304
298.1	−0.491	−0.362	−0.298
303.1	−0.483	−0.356	−0.294
308.1	−0.475	−0.350	−0.289
313.1	−0.468	−0.344	−0.284
		$\varphi_E = 0.10$	
283.1	−0.300	−0.333	−0.274
288.1	−0.295	−0.327	−0.269
293.1	−0.290	−0.322	−0.265
298.1	−0.285	−0.316	−0.260
303.1	−0.280	−0.311	−0.256
308.1	−0.276	−0.306	−0.252
313.1	−0.272	−0.301	−0.248
		$\varphi_E = 0.15$	
283.1	−0.448	−0.337	−0.300
288.1	−0.440	−0.331	−0.295
293.1	−0.433	−0.325	−0.290
298.1	−0.426	−0.320	−0.285
303.1	−0.419	−0.315	−0.280
308.1	−0.412	−0.309	−0.275
313.1	−0.405	−0.305	−0.271

values of theta temperature and entropy of dilution parameter for PEG/PVP blends in mixed water−ethanol are listed in Table 7. The obtained values of entropy of dilution parameter indicate that the entropy of dilution parameter is negative for PEG/PVP blends in all volume fractions of ethanol; that is, solvent molecules are ordered by PEG/PVP blends. However, the absolute value of entropy of dilution parameter for PEG/PVP blends in mixed water−ethanol is less than of that in pure water which is reported previously.[8] The absolute value of entropy of dilution parameter is decreased by increasing the weight ratio of PVP in PEG/PVP blends. This behavior may be due to the interaction of PEG−solvent is stronger than interaction of PVP−water; therefore, the solvent molecules are ordered by PEG rather than by PVP. The heat of dilution parameter for PEG/PVP blends in various volume fractions of ethanol and temperatures were calculated by eq 6. The values of the heat of dilution parameter for PEG/PVP blends in various volume fractions of ethanol and temperatures are listed in Table 8. The obtained results indicate that the heat of dilution parameter is negative in all volume fractions of ethanol; that is, interactions of segment−solvent are favored toward segment−segment. However, the absolute value of heat of dilution parameter for PEG/PVP blends in mixed water−ethanol is less than of that in pure water which reported previously.[8] The absolute values of heat of dilution parameter were decreased by increasing the weight ratio of PVP in PEG/PVP blends. This behavior maybe due to the fact that the interaction of segment−solvent in PEG is stronger than its PVP.

Table 9. Experimental and Ideal Polymer−Solvent Interaction Parameter, χ, of PEG/PVP Blends in Different Solvent Compositions at Different Temperatures

T/K	$\chi_m^{exp} \pm 5\cdot10^{-3}$			$\chi_m^{id} \pm 5\cdot10^{-3}$		
	$W_{PEG} = 0.75$	$W_{PEG} = 0.50$	$W_{PEG} = 0.25$	$W_{PEG} = 0.75$	$W_{PEG} = 0.50$	$W_{PEG} = 0.25$
$\varphi_E = 0.05$						
283.1	0.334	0.361	0.391	0.335	0.361	0.388
288.1	0.343	0.367	0.397	0.342	0.367	0.392
293.1	0.352	0.374	0.402	0.349	0.373	0.396
298.1	0.360	0.380	0.407	0.356	0.378	0.400
303.1	0.368	0.386	0.412	0.362	0.383	0.404
308.1	0.376	0.392	0.417	0.368	0.388	0.408
313.1	0.384	0.397	0.421	0.374	0.393	0.412
$\varphi_E = 0.10$						
283.1	0.342	0.358	0.389	0.330	0.356	0.383
288.1	0.347	0.364	0.394	0.336	0.361	0.387
293.1	0.352	0.369	0.399	0.342	0.366	0.391
298.1	0.357	0.375	0.403	0.347	0.371	0.395
303.1	0.362	0.380	0.407	0.353	0.376	0.399
308.1	0.366	0.385	0.411	0.358	0.380	0.403
313.1	0.371	0.390	0.415	0.363	0.385	0.406
$\varphi_E = 0.15$						
283.1	0.319	0.350	0.377	0.330	0.356	0.381
288.1	0.327	0.356	0.382	0.335	0.36	0.385
293.1	0.334	0.362	0.387	0.340	0.364	0.388
298.1	0.342	0.367	0.392	0.344	0.368	0.391
303.1	0.349	0.373	0.396	0.349	0.372	0.394
308.1	0.355	0.378	0.401	0.353	0.375	0.397
313.1	0.362	0.383	0.405	0.357	0.379	0.400

Table 10. Second Osmotic Virial Coefficient, A, of PEG/PVP Blends in Different Solvent Compositions at Different Temperatures

T/K	$10^3 A_m^{ex} \pm 5\cdot10^{-2}/\mathrm{m}^3\cdot\mathrm{mol}\cdot\mathrm{kg}^{-2}$			$10^3 A_m^{id} \pm 5\cdot10^{-2}/\mathrm{m}^3\cdot\mathrm{mol}\cdot\mathrm{kg}^{-2}$		
	$W_{PEG} = 0.75$	$W_{PEG} = 0.50$	$W_{PEG} = 0.25$	$W_{PEG} = 0.75$	$W_{PEG} = 0.50$	$W_{PEG} = 0.25$
$\varphi_E = 0.05$						
283.1	2.71	2.02	1.46	3.05	2.39	1.74
288.1	2.59	1.94	1.40	2.94	2.31	1.68
293.1	2.48	1.87	1.35	2.84	2.23	1.63
298.1	2.38	1.8	1.29	2.73	2.15	1.57
303.1	2.25	1.73	1.23	2.64	2.08	1.53
308.1	2.15	1.66	1.19	2.54	2.01	1.48
313.1	2.05	1.60	1.14	2.44	1.94	1.43
$\varphi_E = 0.10$						
283.1	2.46	1.94	1.40	2.93	2.31	1.68
288.1	2.40	1.87	1.35	2.85	2.25	1.64
293.1	2.33	1.80	1.31	2.77	2.18	1.59
298.1	2.27	1.75	1.26	2.69	2.12	1.54
303.1	2.21	1.70	1.22	2.62	2.07	1.51
308.1	2.16	1.64	1.18	2.54	2.00	1.46
313.1	2.11	1.59	1.13	2.47	1.94	1.42
$\varphi_E = 0.15$						
283.1	2.59	1.91	1.44	2.76	2.19	1.61
288.1	2.50	1.85	1.39	2.71	2.14	1.58
293.1	2.41	1.79	1.34	2.63	2.08	1.53
298.1	2.33	1.73	1.30	2.57	2.04	1.50
303.1	2.25	1.68	1.26	2.52	2.00	1.47
308.1	2.17	1.64	1.22	2.47	1.95	1.44
313.1	2.09	1.58	1.17	2.41	1.91	1.40

The polymer−solvent interaction parameter was calculated by eq 7. The values of polymer−solvent interaction parameter are listed in Table 9. The results of Table 8 indicate that the polymer−solvent interaction parameter for PEG/PVP blends in all volume fractions of ethanol are increased by increasing temperature. The polymer−solvent interaction parameter is related to the quality of solvent in polymer solutions. A good solvent has a low value of polymer−solvent interaction

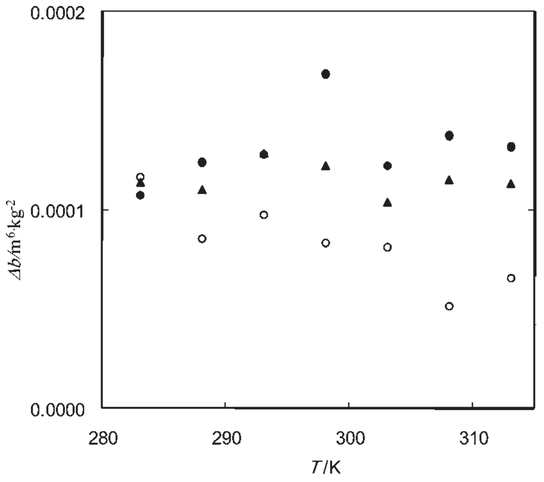

Figure 2. Plots of Δb versus T for blends of PEG/PVP in mixed water−ethanol ($\varphi_E = 0.05$); ●, $w_{PEG} = 0.75$; ○, $w_{PEG} = 0.50$; ▲, $w_{PEG} = 0.25$.

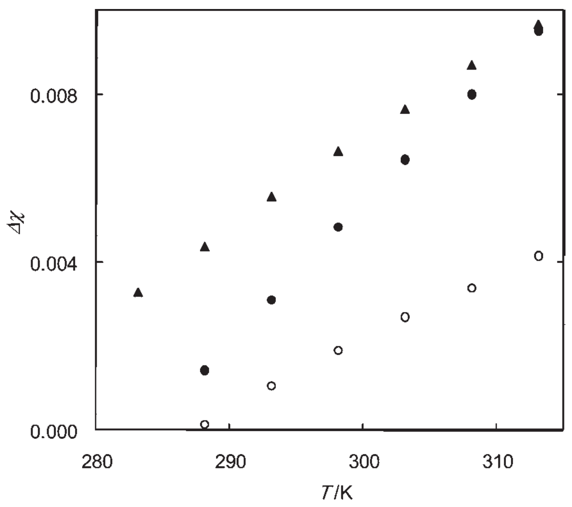

Figure 3. Plots of $\Delta\chi$ versus T for blends of PEG/PVP in mixed water−ethanol ($\varphi_E = 0.05$); ●, $w_{PEG} = 0.75$; ○, $w_{PEG} = 0.50$; ▲, $w_{PEG} = 0.25$.

parameter, while a poor solvent has a high value of polymer−solvent interaction parameter; therefore, the results of Table 9 indicate that the quality of mixed water−ethanol for PEG/PVP blends were decreased by increasing temperature. The polymer−solvent interaction parameters were increased by increasing the weight ratio of PVP in PEG/PVP blends; therefore, the results of Table 9 indicate that the quality of mixed water−ethanol for PEG/PVP blends were decreased by increasing the weight ratio of PVP in PEG/PVP blends.

The second osmotic virial coefficients were calculated by eq 8. The obtained second virial coefficients are listed in Table 10. The second osmotic virial coefficient is related to the quality of solvent in polymer solutions. A good solvent has a positive value of the second osmotic virial coefficient, while a poor solvent has a negative value of the second osmotic virial coefficient; therefore the results of Table 10 indicate that the quality of mixed water−ethanol for PEG/PVP blends was decreased by increasing the temperature and weight ratio of PVP in PEG/PVP blends. Similar behaviors were observed for PEG/PVP blends in water.[8]

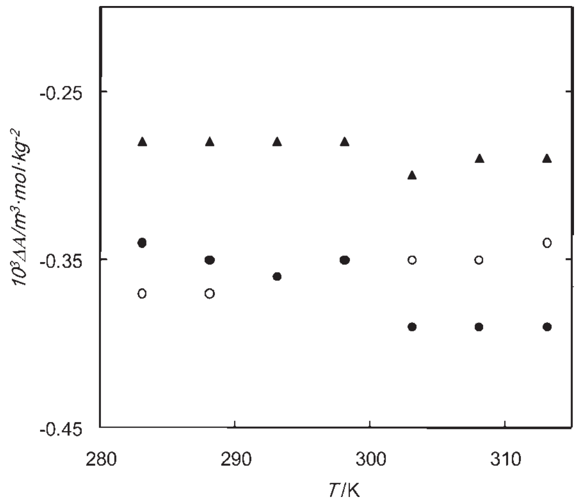

Figure 4. Plots of ΔA versus T for blends of PEG/PVP in mixed water−ethanol ($\varphi_E = 0.05$); ●, $w_{PEG} = 0.75$; ○, $w_{PEG} = 0.50$; ▲, $w_{PEG} = 0.25$.

The compatibility of PEG and PVP was evaluated in terms of the interaction parameter, b, the polymer−solvent interaction parameter, χ, and the second osmotic virial coefficient, A. The ideal values of b_m, χ_m, and A_m parameters for blends were calculated by rgw data of refs 16 and 17 and eqs 11, 12, and 13, respectively. The differences between the experimental and the ideal values of the b parameter for one of the systems are shown in Figure 2. According to the criterion proposed by Garcia et al.,[3] Figure 2 shows that the PEG/PVP blends are compatible. The results of Figure 2 indicate that the compatibility of PEG/PVP blends is not affected considerably by temperature. The differences between the experimental and the ideal values of χ parameter are shown in Figure 3. According to the criterion proposed previously by us, Figure 3 shows that the PEG/PVP blends are compatible. The results of Figure 3 indicate that the compatibility of PEG/PVP blends is affected slightly by temperature. However, according to the criterion based on the χ parameter, the PEG/PVP blends in mixed water−ethanol with $\varphi_E = 0.15$ become compatible at above 300 K. The differences between the experimental and the ideal values of the A parameter are shown in Figure 4. According to the criterion proposed by us, Figure 4 shows that the PEG/PVP blends are compatible. Our previous results reveal that the PEG/PVP blends in water were incompatible.[8] Therefore, the compatibility of polymer blends are dependent on the solvent. It is well-known that water−ethanol solution possesses very strong intermolecular interactions via hydrogen bonding. This has an effect of reducing the strength of solvent−polymer interactions, which, as a consequence, leads to an enhancement of polymer−polymer interaction. Therefore, PEG/PVP blends become compatible in mixed water−ethanol.

■ CONCLUSION

In this work, the effects of temperature and solvent composition on the intrinsic viscosity of PEG/PVP blends were investigated. The polymer solution thermodynamic parameters were evaluated by the temperature dependence of polymer chain expansion factor. The obtained thermodynamic parameters indicate that mixed water−ethanol becomes an increasingly weak solvent for PEG/PVP blends with increasing temperature.

The compatibility of PEG/PVP blends was explained in terms of some thermodynamic parameters. Our results reveal that PEG/PVP blends in mixed water−ethanol are compatible.

AUTHOR INFORMATION

Corresponding Author

*Fax: +98 411 3340191. E-mail: a_mehrdad@tabrizu.ac.ir.

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