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

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In this work, the intrinsic viscosities of poly(ethylene glycol) (PEG) with a molar mass of 20 $\text{kg}\cdot\text{mol}^{-1}$ 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, θ 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 mixtures of water−ethanol are changed to the poorer solvents for PEG by increasing temperature. Also the thermodynamic parameters indicate that water−ethanol mixtures are changed to the poorer solvents for PEG by increasing volume fractions of ethanol.

Introduction

One of the most important transport properties in polymerization processes is the viscosity of polymer solutions.[1] Polymer−solvent and polymer−polymer mixture viscosity is an important physical property in polymer research, development, and engineering.[2] When high molecular weight nonionic polymer molecules dissolve in a fluid, they typically expand to form spherical coils. In dilute solutions, the volume associated with each polymer coil contains one polymer molecule surrounded by a much larger mass of solvent. A polymer coil's hydrodynamic volume depends upon the polymer molecular weight and its thermodynamic interaction with the solvent. Favorable polymer−solvent interactions also increase the hydrodynamic volume of the polymer coil. When the polymer−solvent interactions are unfavorable, the polymer coil volume is decreased. With unfavorable polymer−solvent interactions, polymer coils can completely collapse and become insoluble in the fluid. Polymer−solvent interactions depend upon the polymer molecular structure, chemical composition, solution concentration, solvent molecular structure, and the solution temperature.[3]

Poly(oxyethylene), an industrially important polymer, has unique solubility properties, dissolving in water in all proportions at moderate temperatures and in a very wide range of degrees of polymerization, contrary to other structurally similar polyethers, which are all insoluble in water. Poly(oxyethylene) has two names. The low and high molecular weights of poly(oxyethylene) are named poly(ethylene glycol) (PEG) and poly(ethylene oxide) (PEO), respectively. It is expected that the structure of water would affect the conformation of poly(oxyethylene) in aqueous solution and play an important role in the physicochemical properties of the solution.[4] Therefore, a significant amount of research has been conducted with regard to studying poly(oxyethylene) solutions which for the majority of these studies are in water and aqueous salt solutions.[4−9] The previous findings indicate that water is a good solvent for PEO at low temperatures and water approaches a θ solvent for PEO with increasing temperature.[10,11] The previous findings indicate that a water−ethanol mixture is a poorer solvent for PEO than pure water.[9,12] The aim of this study was to determine the effect of temperature on the intrinsic viscosities of PEG in mixtures of water + ethanol and calculate some of the thermodynamic parameters by temperature dependence of the expansion factor of the polymer chain.

Theoretical

The reduced viscosity of dilute macromolecular solutions, η_{red}, is given by:

$$\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{C} = \frac{\eta - \eta_0}{\eta_0 C} = \frac{td - t_0 d_0}{t_0 d_0 C} \tag{1}$$

where η_{sp} is specific viscosity, t and t_0 are the flow times for the given polymer solution and the solvent, η and η_0 are the viscosities of the given polymer solution and the solvent, d and d_0 are the densities for the given polymer solution and the solvent, and C is the solution concentration. The plot of reduced viscosity versus concentration in dilute solution often gives a straight line, and Huggins proposed the below equation.[13]

$$\eta_{\text{red}} = [\eta] + k_{\text{H}}[\eta]^2 C \tag{2}$$

where $[\eta]$ and k_{H} are the intrinsic viscosity and Huggins constant, respectively. Some other equations for the determination of $[\eta]$ are Schultz−Blaschke and Kraemer

$$\eta_{\text{red}} = [\eta] + k_{\text{SB}}[\eta]\eta_{\text{sp}} \tag{3}$$

$$\frac{\ln(\eta_{\text{sp}} + 1)}{C} = [\eta] + k_{\text{K}}[\eta]^2 C \tag{4}$$

where k_{SB} and k_{K} are the Schultz−Blaschke and Kraemer constants, respectively.

In a good solvent the polymer molecule expands. The expansion factor, α, which describes the excluded volume effect, is given by:[14]

$$\alpha = \left(\frac{\langle R^2\rangle}{\langle R^2\rangle_0}\right)^{0.5} \tag{5}$$

where $\langle R^2\rangle$ and $\langle R^2\rangle_0$ are the mean square end-to-end distances of a polymer chain in expanded and in unperturbed chains,

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respectively. Flory and Fox suggested that the Mark−Houwink equation can be put in the form:[15]

$$[\eta] = KM^{0.5}\alpha^3 \tag{6}$$

where M is the molecular weight of polymer and K is given by:

$$K = \Phi\left(\frac{\langle R^2\rangle}{M\alpha^2}\right)^{1.5} = \Phi\left(\frac{\langle R^2\rangle_0}{M}\right)^{1.5} \tag{7}$$

where Φ is the Flory constant. The Flory constant is equal to $2.8 \cdot 10^{20}$.[4] Therefore, substituting eq 7 in eq 6 yields:

$$\alpha^3 = \frac{[\eta]M}{\Phi\langle R^2\rangle_0^{\,1.5}} \tag{8}$$

In the random flight chains model with restricted bond angles ϕ where rotations about the bonds are not restricted, $\langle R^2\rangle_0$ is given by:[16]

$$\langle R^2\rangle_0 = Nl^2\,\frac{1-\cos\phi}{1+\cos\phi} + 2l^2\cos\phi\,\frac{1+(\cos\phi)^N}{(1+\cos\phi)^2} \tag{9}$$

where N and l are the number of bonds existing in polymer chain and the bond length, respectively. However, in the case of PEG $\phi = 109.5°$, and the value of N is the two-fold of ratio molecular mass of polymer to mass of monomer, because there are two linkages in each monomer of PEG. The value of l in the case of PEG is derived by taking the average from bond length for (C−C) and (C−O). The used bonds length are $l_{\mathrm{C-C}} = 0.153$ nm and $l_{\mathrm{C-O}} = 0.143$ nm.[8]

Therefore, substituting eq 9 in eq 8 yields:

$$\alpha^3 = \frac{[\eta]M}{\Phi}\left(Nl^2\,\frac{1-\cos\phi}{1+\cos\phi} + 2l^2\cos\phi\,\frac{1+(\cos\phi)^N}{(1+\cos\phi)^2}\right)^{-1.5} \tag{10}$$

Flory and Fox further suggested that the temperature dependence of the expansion factor is as follows:[15]

$$\alpha^5 - \alpha^3 = \left(\frac{27}{2^{1.5}\pi^{1.5}}\right)\left(\frac{\bar{v}^2}{N_A V_s}\right)\left(\frac{\langle R^2\rangle_0}{M}\right)^{-1.5}\Psi M^{0.5}\left(1-\frac{\theta}{T}\right) \tag{11}$$

where V_s, $\bar{v}$, N_A, and T are the molar volume of solvent, the partial specific volume of the polymer, Avogadro's number, and the absolute temperature, respectively. On the other hand, the relation of Ψ and κ is given by:[17]

$$\kappa = \frac{\theta\Psi}{T} \tag{12}$$

where thermodynamic parameters Ψ, κ, and θ are the entropy of dilution parameter, the heat of dilution parameter, and θ temperature, respectively. The polymer−solvent interaction parameter, χ, can be expressed in terms of entropy and heat of dilution parameter as:[17]

$$\chi = 0.5 + \kappa - \Psi \tag{13}$$

On the other hand, the temperature dependence of the polymer−solvent interaction parameter is as follows:[4]

$$\chi = \chi_S + \frac{\chi_H}{T} \tag{14}$$

where χ_S and χ_H are the entropic and enthalpic contribution of polymer−solvent interaction parameter, respectively. 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:[17]

$$A = \frac{\bar{v}^2}{V_s}(\Psi - \kappa)F(\alpha) \tag{15}$$

where

$$F(\alpha) = \sum_{n=0}^{\infty}\frac{[-2(\alpha^2-1)]^n}{(n+1)!(n+1)^{1.5}} \tag{16}$$

Experimental Section

Materials. The PEG used in this study was purchased from Merck Chemical Co. and had a reported nominal molar mass of 20 kg·mol^{-1}. Ethanol was purchased from Merck Chemical Co. and had a reported mass fraction purity of 0.995. PEG 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 a molar mass of 21.2 kg·mol^{-1} with a polydispersity index of 1.20 for PEG. PEG solutions were prepared gravimetrically by an analytical balance (Sartorius CP224 S) with an uncertainty of $\pm\, 2 \cdot 10^{-7}$ kg into preprepared ethanol aqueous solutions with volume fractions of ethanol of $\varphi_E = 0.05$, 0.10, 0.15, and 0.20. The uncertainties of the ethanol volume fractions and concentration of polymer solutions are ± 0.2 % and $\pm\, 5 \cdot 10^{-3}$ kg·m^{-3}, respectively. The polymer solutions were filtered before use by a filter with an aperture of 75 μm, and their 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. Densities were measured with a U-tube vibrating densimeter (Kyoto Electronic DA-210) with an uncertainty of $\pm\, 3 \cdot 10^{-2}$ kg·m^{-3}. The flow times for solutions which used in this work were never less than 200 s with an uncertainty of ± 0.2 s; therefore, the maximum uncertainty of viscosity was ± 0.3 %.

Results and Discussion

The flow times of solutions of PEG in ethanol aqueous solutions with volume fractions of ethanol of $\varphi_E = 0.05$, 0.10, 0.15, and 0.20 were measured at various temperatures and concentrations of polymer, and from these data, specific viscosities, η_{sp}, are calculated. The calculated specific viscosities in various conditions are listed in Table 1. According to the Huggins equation, the intrinsic viscosity of the polymer is obtained by extrapolation of reduced viscosity to zero polymer concentration. The obtained intrinsic viscosities according to the Huggins equation with uncertainties of ± 0.00005 m^3·kg^{-1} and Huggins constants with uncertainties of ± 0.001 are listed in Tables 2 and 3. According to the Schultz−Blaschke equation, the intrinsic viscosity of the polymer is obtained by extrapolation of reduced viscosity to zero specific viscosity. The obtained intrinsic viscosities according to the Schultz−Blaschke equation with uncertainties of ± 0.00005 m^3·kg^{-1} and Schultz−Blaschke constants with uncertainties of ± 0.001 are listed in Tables 2 and 3. Also, according to the Kraemer equation, the intrinsic viscosity of the polymer is obtained by extrapolation of $[Ln(\eta_{sp} + 1)]/C$ to zero polymer concentration. The obtained

Table 1. Specific Viscosities, η_{sp}, of PEG in a Mixture of Water and Ethanol at Different Temperatures

C	η_{sp}						
$kg \cdot m^{-3}$	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
				$\varphi_E = 0.05$			
2.04		0.0860	0.0839				
3.95	0.1751	0.1710	0.1660	0.1627	0.1579	0.1534	0.1491
6.10	0.2795	0.2715	0.2626	0.2573	0.2502	0.2418	0.2355
7.97	0.3698	0.3595	0.3499	0.3420	0.3321	0.3227	0.3133
10.00	0.4792	0.4659	0.4525	0.4423	0.4274	0.4142	0.4005
11.94	0.5832	0.5655	0.5515	0.5371	0.5215	0.5047	0.4893
13.97	0.6989	0.6785	0.6602	0.6421	0.6230	0.6040	0.5853
15.99	0.8199	0.7954	0.7725	0.7507	0.7270	0.7024	0.6792
18.00	0.9439	0.9150	0.8889	0.8643	0.8376	0.8094	0.7855
19.99	1.0751	1.0370	1.0084	0.9814	0.9492	0.9175	0.8883
				$\varphi_E = 0.10$			
4.03	0.1751	0.1713	0.1683	0.1645	0.1599	0.1567	0.1535
5.95	0.2646		0.2520	0.2483	0.2424	0.2380	0.2329
7.91	0.3605	0.3513	0.3445	0.3374	0.3293	0.3207	0.3151
9.92	0.4619	0.4526	0.4424	0.4330	0.4225	0.4133	0.4038
11.90	0.5666	0.5547	0.5446	0.5300	0.5173	0.5052	0.4935
13.83	0.6762	0.6601	0.6457	0.6309	0.6133	0.5972	0.5842
15.94	0.7973	0.7798	0.7622	0.7442	0.7240	0.7050	0.6889
				$\varphi_E = 0.15$			
4.06	0.1697	0.1666	0.1654	0.1617	0.1585	0.1550	
6.01	0.2560	0.2536	0.2492	0.2455	0.2413		0.2318
7.89	0.3449	0.3420	0.3384	0.3316	0.3253	0.3187	0.3127
9.95	0.4472	0.4414	0.4359	0.4279	0.4211	0.4114	0.4023
11.87	0.5479	0.5425	0.5353	0.5249	0.5174	0.5071	0.4967
13.87	0.6567	0.6510	0.6409	0.6269	0.6166	0.6032	0.5907
15.70	0.7595	0.7506	0.7393	0.7242	0.7104	0.6947	0.6807
17.79	0.8796	0.8716	0.8587	0.8427	0.8266	0.8075	0.7900
				$\varphi_E = 0.20$			
1.97	0.0797	0.0785	0.0774	0.0761	0.0749	0.0738	0.0724
2.94	0.1196		0.1165	0.1147	0.1137		0.1103
3.90	0.1598	0.1177	0.1553	0.1540	0.1535	0.1505	0.1485
4.94	0.2045	0.2026	0.2007	0.1988	0.1973	0.1938	0.1902
5.86	0.2457	0.2445	0.2420	0.2397	0.2349	0.2326	0.2288
6.85		0.2874	0.2859	0.2827	0.2797		0.2713
7.85	0.3364	0.3335		0.3287	0.3258	0.3186	0.3142
8.89	0.3853	0.3810	0.3785	0.3738	0.3728	0.3686	0.3628
9.81	0.4273	0.4253	0.4225	0.4169	0.4122	0.4100	0.4053

Table 2. Intrinsic Viscosities, [η], of PEG in Various Mixtures of Water and Ethanol at Different Temperatures on the Basis of Huggins, Schultz−Blaschke, and Kraemer Equations

T/K	$\varphi_E = 0.05$	$\varphi_E = 0.10$	$\varphi_E = 0.15$	$\varphi_E = 0.20$
	$[\eta]/m^3 \cdot kg^{-1}$ According to the Huggins Equation			
283.1	0.04194	0.04098	0.03915	0.03921
288.1	0.04102	0.04008	0.03861	0.03868
293.1	0.03992	0.03934	0.03830	0.03808
298.1	0.03919	0.03875	0.03764	0.03762
303.1	0.03816	0.03786	0.03703	0.03722
308.1	0.03713	0.03730	0.03635	0.03656
313.1	0.03619	0.03668	0.03592	0.03598
	$[\eta]/m^3 \cdot kg^{-1}$ According to the Schultz−Blaschke Equation			
283.1	0.04265	0.04148	0.03978	0.03933
288.1	0.04151	0.04057	0.03926	0.03881
293.1	0.04040	0.03981	0.03892	0.03825
298.1	0.03975	0.03917	0.03825	0.03779
303.1	0.03868	0.03827	0.03763	0.03740
308.1	0.03762	0.03766	0.03694	0.03678
313.1	0.03665	0.03701	0.03657	0.03620
	$[\eta]/m^3 \cdot kg^{-1}$ According to the Kraemer Equation			
283.1	0.04178	0.04089	0.03919	0.03913
288.1	0.04088	0.04002	0.03870	0.03863
293.1	0.03983	0.03930	0.03837	0.03808
298.1	0.03904	0.03867	0.03772	0.03762
303.1	0.03802	0.03779	0.03712	0.03724
308.1	0.03701	0.03720	0.03644	0.03664
313.1	0.03609	0.03657	0.03600	0.03608

Table 3. Huggins Constant, k_H, Schultz−Blaschke Constant, k_{SB}, and Kraemer Constant, k_K, of PEG in Various Mixtures of Water and Ethanol at Different Temperatures

T/K	$\varphi_E = 0.05$	$\varphi_E = 0.10$	$\varphi_E = 0.15$	$\varphi_E = 0.20$
		k_H		
283.1	0.326	0.327	0.370	0.276
288.1	0.318	0.337	0.387	0.307
293.1	0.327	0.340	0.379	0.347
298.1	0.319	0.330	0.384	0.365
303.1	0.321	0.334	0.393	0.383
308.1	0.322	0.319	0.397	0.419
313.1	0.322	0.317	0.386	0.442
		k_{SB}		
283.1	0.241	0.255	0.276	0.243
288.1	0.243	0.262	0.286	0.269
293.1	0.250	0.265	0.283	0.298
298.1	0.241	0.259	0.287	0.313
303.1	0.244	0.264	0.293	0.327
308.1	0.246	0.255	0.297	0.352
313.1	0.248	0.255	0.286	0.370
		k_K		
283.1	−0.158	−0.161	−0.140	−0.201
288.1	−0.164	−0.157	−0.132	−0.180
293.1	−0.160	−0.156	−0.136	−0.154
298.1	−0.163	−0.161	−0.133	−0.141
303.1	−0.162	−0.158	−0.129	−0.129
308.1	−0.162	−0.166	−0.126	−0.107
313.1	−0.163	−0.167	−0.132	−0.091

intrinsic viscosities according to the Kraemer equation with uncertainties of ± 0.00005 $m^3 \cdot kg^{-1}$ and Kraemer constants with uncertainties of ± 0.001 are listed in Tables 2 and 3. A comparison of the results of Table 2 reveals that the obtained

Table 4. Expansion Factor, α, of PEG in Various Mixtures of Water and Ethanol at Different Temperatures

T	α			
K	$\varphi_E = 0.05$	$\varphi_E = 0.10$	$\varphi_E = 0.15$	$\varphi_E = 0.20$
283.1	1.903	1.889	1.860	1.861
288.1	1.889	1.875	1.852	1.853
293.1	1.872	1.863	1.847	1.843
298.1	1.861	1.854	1.836	1.836
303.1	1.844	1.840	1.826	1.829
308.1	1.828	1.831	1.815	1.818
313.1	1.812	1.820	1.808	1.809

Table 5. Heat of Dilution Parameter, *κ*, in Various Mixtures of Water and Ethanol at Different Temperatures

T	*κ*			
K	$\varphi_E = 0.05$	$\varphi_E = 0.10$	$\varphi_E = 0.15$	$\varphi_E = 0.20$
283.1	−0.4962	−0.3974	−0.3210	−0.3293
288.1	−0.4876	−0.3905	−0.3154	−0.3235
293.1	−0.4792	−0.3838	−0.3100	−0.3180
298.1	−0.4712	−0.3774	−0.3048	−0.3127
303.1	−0.4634	−0.3711	−0.2998	−0.3075
308.1	−0.4559	−0.3651	−0.2949	−0.3025
313.1	−0.4486	−0.3593	−0.2902	−0.2977

Table 6. Polymer−Solvent Interaction Parameter, *χ*, in Various Mixtures of Water and Ethanol at Different Temperatures

T	*χ*			
K	$\varphi_E = 0.05$	$\varphi_E = 0.10$	$\varphi_E = 0.15$	$\varphi_E = 0.20$
283.1	0.3081	0.3031	0.3046	0.2912
288.1	0.3167	0.3100	0.3102	0.2969
293.1	0.3250	0.3166	0.3155	0.3024
298.1	0.3330	0.3231	0.3207	0.3078
303.1	0.3408	0.3293	0.3258	0.3129
308.1	0.3483	0.3353	0.3306	0.3179
313.1	0.3556	0.3412	0.3353	0.3227

intrinsic viscosities from Huggins, Schultz−Blaschke, and Kraemer equations are comparable. The obtained intrinsic viscosities of PEG are decreased by increasing temperature and volume fraction of ethanol. Therefore, ethanol aqueous solutions were changed to the poorer solvents for PEG by increasing temperature and volume fraction of ethanol. These finds are consistent with the results of other investigators.[9] The values of the expansion factor were calculated using intrinsic viscosities which are obtained on the basis of the Huggins equation. The calculated expansion factors of PEG at different temperatures and various volume fractions of ethanol are listed in Table 4. The data of Table 4 indicate that the values of expansion factor were decreased by increasing temperature. This behavior is maybe due to the effect of temperature on the interactions of segment−segment and segment−solvent. The interaction of segment−segment is favored toward segment−solvent by increasing temperature; therefore, the chain of PEG shrinks, and the end-to-end distance becomes smaller by increasing temperature. For evaluating the *θ* 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 *θ* temperature and entropy of dilution parameter were calculated. The obtained values of *θ* temperature for ethanol aqueous solutions with volume fractions of ethanol of $\varphi_E = 0.05$, 0.10, 0.15, and 0.20 are (462, 561, 724, and 774) K, respectively. The obtained values of the entropy of dilution parameter for PEG in mixtures of water and ethanol with the volume fractions of $\varphi_E = 0.05$, 0.10, 0.15, and 0.20 are −0.3042, −0.2005, −0.1256, and −0.1205, respectively. The obtained values of the entropy of dilution parameter indicate that the entropy of dilution parameter is negative for PEG in all volume fractions of ethanol, that is, solvent molecules are ordered by PEG. However, the absolute value of the entropy of dilution parameter is decreased by increasing volume fractions of ethanol. This behavior is maybe due to the interaction of PEG−water being stronger than interaction of PEG−ethanol; therefore, the water molecules rather than ethanol are ordered by PEG. The values of the heat of dilution parameter for PEG in various volume fractions of ethanol and temperatures were calculated by eq 12, and these values are listed in Table 5. The obtained values of the heat of dilution parameter indicate that the heat of dilution parameter is negative for PEG in all volume fractions of ethanol, that is, interactions of segment−solvent are favored toward segment−segment in PEG. However, the absolute value of the heat of dilution parameter is decreased by increasing the volume fractions of ethanol. This behavior is maybe due to the interaction of segment−water which is stronger than its segment−ethanol. The values of the polymer−solvent interaction parameter are calculated by eq 13, and these values are listed in Table 6. The results of Table 6 indicate that the polymer−solvent interaction parameter for PEG 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 the polymer−solvent interaction parameter, while a poor solvent has a high value of the polymer−solvent interaction parameter; therefore, the results of Table 6 indicate that the quality of mixtures of water and ethanol were decreased for solutions of PEG by increasing temperature. By considering eq 14 the plots of χ versus $1/T$ gives the values of χ_S and χ_H. The plots of χ versus $1/T$ are presented in Figure 2. The obtained values of χ_S for PEG in ethanol aqueous solutions with volume fractions of ethanol of $\varphi_E = 0.05$, 0.10, 0.15, and 0.20 are 0.804, 0.700, 0.626, and 0.620, respectively. The obtained values of χ_H for PEG in mixtures of water and ethanol with the volume fractions of $\varphi_E = 0.05$, 0.10, 0.15, and 0.20 are (−140.5, −112.5, −90.9, and −93.2) K, respectively. The strong temperature dependency of segment−segment and segment−solvent interactions corresponds to the higher absolute values of χ_H; therefore, the temperature dependency of segment−segment and segment−solvent interactions is decreased by increasing volume fractions of ethanol. Also the previous findings reveal that the viscosity of PEO shows a stronger temperature dependence in mixed water−ethanol than in pure water.[9] The second osmotic virial coefficients were calculated by eq 15. The obtained second

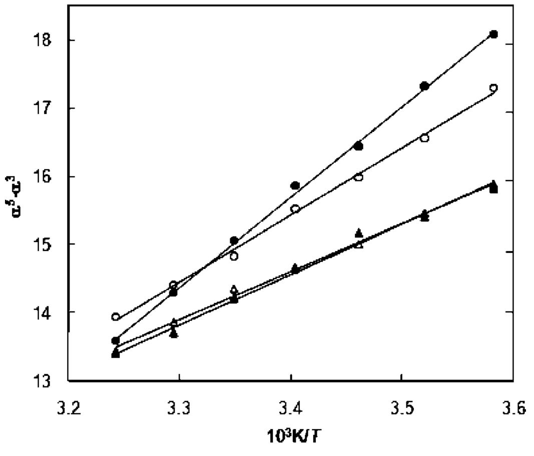

Figure 1. Plots of $(\alpha^5 - \alpha^3)$ versus $1/T$ for PEG in water−ethanol with various volume fractions. ●, $\varphi_E = 0.05$; ○, $\varphi_E = 0.10$; ▲, $\varphi_E = 0.15$; △, $\varphi_E = 0.20$.

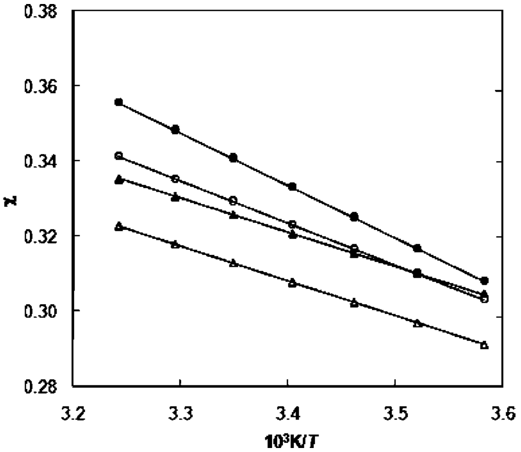

Figure 2. Plots of χ versus $1/T$ for PEG in water−ethanol with various volume fractions. ●, $\varphi_E = 0.05$; ○, $\varphi_E = 0.10$; ▲, $\varphi_E = 0.15$; △, $\varphi_E = 0.20$.

Table 7. Second Osmotic Virial Coefficient, *A*, in Various Mixtures of Water and Ethanol at Different Temperatures

T	$10^3A/\text{m}^3\cdot\text{mol}\cdot\text{kg}^{-2}$			
K	$\varphi_E = 0.05$	$\varphi_E = 0.10$	$\varphi_E = 0.15$	$\varphi_E = 0.20$
283.1	3.70	3.55	3.34	3.34
288.1	3.57	3.46	3.27	3.26
293.1	3.44	3.36	3.18	3.19
298.1	3.31	3.26	3.11	3.12
303.1	3.19	3.18	3.05	3.05
308.1	3.07	3.08	2.98	2.99
313.1	2.95	2.99	2.91	2.93

virial coefficients are listed in Table 7. 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 7 indicate that the quality of mixtures of water and ethanol were decreased for solutions of PEG by increasing temperature and were decreased slightly by increasing the volume fractions of ethanol.

Conclusion

In this work, the effect of temperature and solvent composition on the intrinsic viscosity of PEG was investigated. The polymer solution thermodynamic parameters were evaluated by the temperature dependence of the polymer chain expansion factor. The obtained thermodynamic parameters indicate that mixtures of water and ethanol become an increasingly poor solvent for PEG with increasing temperature and volume fraction of ethanol.

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