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

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In this work, the intrinsic viscosities of poly(vinyl pyrrolidone) with molar mass of 58 $\text{kg}\cdot\text{mol}^{-1}$ 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, 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 mixtures of water/ethanol are changed to the poorer solvents for poly(vinyl pyrrolidone) by increasing temperature. Also, the thermodynamic parameters indicate that water/ethanol are changed to the better solvents for poly(vinyl pyrrolidone) 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 solution temperature.[3]

Poly(vinyl pyrrolidone) (PVP), a water-soluble synthetic polymer, has a number of interesting properties and frequently has been the object of different investigations to understand the interactions, hydrogen bonding, dipole−dipole, ion−dipole, etc., between small organic molecules and ionic species and a polymer.[4] Therefore, a significant amount of research has been conducted with regard to studying poly(vinyl pyrrolidone) solutions, and the majority of these studies are in water, nonionic aqueous solutions, and aqueous salts solutions.[4−9] The previous findings indicate that the intrinsic viscosity of PVP was decreased by increasing temperature.[7,8] The previous findings indicate that addition of ionic and nonionic solutes to aqueous PVP solutions disrupted hydrogen bonds or molecular association of polymers.[4−6] Therefore, thermodynamic parameters such as theta temperature can be affected by ionic and nonionic solutes. The aim of this study was to determine the effect of temperature on the intrinsic viscosities of PVP in mixtures of water + ethanol and to calculate some of the thermodynamic parameters by temperature dependence of the expansion factor of the polymer chain.

Theoretical Section

The reduced viscosity of dilute macromolecular solutions, η_{red}, is given by[10]

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

where η_{sp} is specific viscosity; t and t_0 are the flow time for the given polymer solution and the solvent; η and η_0 are viscosity of the given polymer solution and the solvent; d and d_0 are the density for the given polymer solution and the solvent; and C is solution concentration. The plot of reduced viscosity versus concentration in dilute solution often gives a straight line, and Huggins proposed the below equation.[11]

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

where $[\eta]$ and k_{H} are intrinsic viscosity and Huggins constant, respectively. The other equation for determination of $[\eta]$ is the Kraemer equation.[12]

$$\frac{\ln(\eta_{\text{sp}} + 1)}{C} = [\eta] + k_{\text{K}}[\eta]^2 C \tag{3}$$

where k_{K} is the Kraemer constant.

In a good solvent, the polymer molecule expands. The expansion factor, α, which describes the excluded volume effect, is given by[13]

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$$\alpha = \left(\frac{\langle R^2\rangle}{\langle R^2\rangle_0}\right)^{0.5} \tag{4}$$

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 chain, respectively. Flory and Fox suggested that the Mark−Houwink equation can be put in the form[14]

$$[\eta] = KM^{0.5}\alpha^3 \tag{5}$$

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

$$K = \Phi\left(\frac{\langle R^2\rangle}{M\alpha^2}\right)^{1.5} = \Phi\left(\frac{\langle R^2\rangle_0}{M}\right)^{1.5} \tag{6}$$

where Φ is the Flory constant. The Flory constant is equal $2.8\cdot 10^{20}$.[4] Therefore, substituting eq 6 into eq 5 yields

$$\alpha^3 = \frac{[\eta]M}{\Phi\langle R^2\rangle_0^{1.5}} \tag{7}$$

In the random flight chains model with restricted bond angles ϕ but rotations about the bonds are not restricted, $\langle R^2\rangle_0$ is given by[15]

$$\langle R^2\rangle_0 = Nl^2\frac{1-\cos\phi}{1+\cos\phi} + 2l^2\cos\phi\frac{1+(\cos\phi)^N}{(1+\cos\phi)^2} \tag{8}$$

where N and l are the number of bonds existing in the polymer chain and the bond length, respectively. However, in the case PVP $\phi = 109.5°$ and the value of N is 2-fold the ratio of molecular mass of polymer to mass of monomer, there are two linkages in each monomer of PVP. The value of l in the case of PVP is equal to the bond length of (C−C). The used bond length is $l_{\mathrm{C-C}} = 0.153$.[16]

Therefore, substituting eq 8 into eq 7 yields

$$\alpha^3 = \frac{[\eta]M}{\Phi}\left(Nl^2\frac{1-\cos\phi}{1+\cos\phi} + 2l^2\cos\phi\frac{1+(\cos\phi)^N}{(1+\cos\phi)^2}\right)^{-1.5} \tag{9}$$

Flory and Fox further suggested the temperature dependence of the expansion factor as follows[14]

$$\alpha^5 - \alpha^3 = \left(\frac{27}{2^{1.5}\pi^{1.5}}\right)\left(\frac{\bar{\nu}^2}{N_A V_s}\right)\left(\frac{\langle R^2\rangle_0}{M}\right)^{-1.5}\Psi M^{0.5}\left(1-\frac{\theta}{T}\right) \tag{10}$$

where V_s, $\bar{\nu}$, N_A, and T are the molar volume of solvent, the partial specific volume of the polymer, Avogadro's number, and absolute temperature, respectively. On the other hand, the relation of Ψ and κ is given by[10]

$$\kappa = \frac{\theta\Psi}{T} \tag{11}$$

where thermodynamic parameters Ψ, κ, and θ are the entropy of dilution parameter, the heat of dilution parameter, and theta temperature, respectively. The polymer−solvent interaction parameter, χ, can be expressed in terms of entropy and heat of dilution parameter as[10]

$$\chi = 0.5 + \kappa - \Psi \tag{12}$$

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[10]

$$A = \frac{\bar{\nu}^2}{V_s}(\Psi - \kappa)F(\alpha) \tag{13}$$

where

$$F(\alpha) = \sum_{n=0}^{\infty}\frac{(-2(\alpha^2-1))^n}{(n+1)!(n+1)^{1.5}} \tag{14}$$

Experimental Section

Materials. The poly(vinyl pyrrolidone) used in this study was purchased from Fluka Chemical Co. and had a reported nominal average molar mass of 58 $\mathrm{kg\cdot mol^{-1}}$. Ethanol was purchased from Merck Chemical Co. and had a reported mass fraction purity of 0.995. Poly(vinyl pyrrolidone) and ethanol were used without further purification. Distilled water was used for 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 56.3 $\mathrm{kg\cdot mol^{-1}}$ with polydispersity index 1.25 for PVP. PVP solutions were prepared gravimetrically by an analytical balance (Sartorius CP224 S) with an uncertainty $\pm\, 2\cdot 10^{-7}$ kg and were dispersed into preprepared ethanol aqueous solutions with volume fractions of ethanol $\varphi_E = 0.05$, 0.10, 0.15, and 0.20. The uncertainties of the ethanol volume fractions and concentration of polymer solutions are ± 0.2 % and $\pm\, 5\cdot 10^{-3}\ \mathrm{kg\cdot m^{-3}}$, respectively. The polymer solutions were filtered before use by a filter with aperture 75 μm, and their viscosities were measured using a jacketed Ubbelohde viscometer with 0.4 mm capillary. The temperature of solutions was kept constant by a temperature controller (Eyela, UA-10, Tokyo Rikakiai Co.) with an uncertainty ± 0.1 K. Densities were measured with a U-tube vibrating densimeter (Kyoto Electronic DA-210) with an uncertainty $\pm\, 3\cdot 10^{-2}\ \mathrm{kg\cdot m^{-3}}$. The flow times for solutions which were used in this work were never less than 180 s. The flow times were determined from an average three readings with uncertainty of ± 0.2 s.

Results and Discussion

The flow times of solutions of PVP in ethanol aqueous solutions with volume fractions of ethanol $\varphi_E = 0.05$, 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.

Table 1. Specific Viscosities, η_{sp}, of PVP with Uncertainty ± $5 \cdot 10^{-4}$ in Mixtures of Water and Ethanol at Different Temperatures

	η_{sp}						
$C/\text{kg}\cdot\text{m}^{-3}$	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
				$\varphi_E = 0.05$			
2.02	0.0511	0.0503	0.0493	0.0486	0.0475	0.0463	0.0452
3.96	0.1027	0.1005	0.0985	0.0969	0.0949	0.0920	0.0900
6.00	0.1590	0.1562	0.1524	0.1494	0.1463	0.1431	0.1392
7.96	0.2151	0.2094	0.2057	–	0.1968	0.1910	0.1872
9.89	0.2728	0.2664	0.2593	0.2552	0.2485	0.2414	0.2363
11.87	0.3345	0.3264	0.3173	0.3113	0.3030	0.2958	0.2871
13.90	0.3973	0.3879	0.3781	0.3700	0.3609	0.3511	0.3426
15.99	0.4662	0.4532	0.4420	0.4327	0.4232	0.4109	0.4009
17.92	0.5331	0.5195	0.5046	0.4946	0.4824	0.4700	0.4559
				$\varphi_E = 0.10$			
5.96	0.1577	0.1530	0.1507	0.1464	0.1423	0.1398	0.1371
7.91	0.2129	0.2075	0.2039	0.1985	0.1937	0.1895	0.1866
9.99	0.2746	0.2672	0.2626	0.2567	0.2507	0.2446	0.2412
11.95	0.3364	0.3247	0.3185	0.3115	0.3048	0.2977	0.2936
13.87	0.4004	0.3845	0.3764	0.3685	0.3608	0.3529	0.3488
15.79	0.4613	0.4493	0.4377	0.4320	0.4227	0.4093	0.4036
17.62	0.5258	0.5089	0.4965	0.4862	0.4754	0.4637	0.4561
19.72	0.5986	0.5798	0.5644	0.5540	0.5418	0.5286	0.5194
				$\varphi_E = 0.15$			
5.95	0.1540	0.1518	0.1496	0.1468	0.1435	0.1404	0.1387
7.62	0.2002	0.1980	0.1955	0.1904	0.1877	0.1837	0.1810
9.92	0.2664	0.2635	0.2611	0.2558	0.2510	0.2464	0.2414
11.80	0.3226	0.3183	0.3133	0.3065	0.3014	0.2992	0.2931
13.86	0.3883	0.3831	0.3765	0.3700	0.3644	0.3579	0.3509
15.73	0.4506	0.4435	0.4375	0.4296	0.4225	0.4148	0.4082
17.58	0.5132	0.5058	0.5017	0.4910	0.4834	0.4722	0.4644
19.72	0.5862	0.5791	0.5726	0.5641	0.5544	0.5423	0.5307
				$\varphi_E = 0.20$			
2.94	0.0750	0.0733	0.0718	0.0694	0.0682	0.0669	0.0656
3.91	0.1007	0.0987	0.0962	0.0942	0.0913	0.0906	0.0892
4.88	0.1271	0.1243	0.1202	0.1177	0.1161	0.1140	0.1126
5.88	0.1543	0.1494	0.1466	0.1434	0.1414	0.1380	0.1357
6.88	0.1822	0.1759	0.1727	0.1692	0.1654	0.1633	0.1626
7.83	0.2104	0.2052	0.1996	0.1958	0.1916	0.1882	0.1849
8.80	0.2383	0.2332	0.2263	0.2232	0.2178	0.2123	0.2106
9.76	0.2642	0.2570	0.2537	0.2486	0.2457	0.2414	–
10.71	0.2941	0.2856	0.2823	0.2760	0.2725	0.2679	0.2619
11.72	0.3262	0.3176	0.3097	0.3044	0.3001	0.2970	0.2882
12.54	0.3521	0.3386	0.3326	0.3277	0.3227	0.3159	0.3132

Table 2. Intrinsic Viscosities, [η], of PVP with Uncertainty ± $5 \cdot 10^{-5}$ $\text{m}^3 \cdot \text{kg}^{-1}$ in Various Mixtures of Water and Ethanol at Different Temperatures on the Basis of Huggins and Kraemer Equations

T/K	$\varphi_E = 0.05$	$\varphi_E = 0.10$	$\varphi_E = 0.15$	$\varphi_E = 0.20$
	$[\eta]/\text{m}^3\cdot\text{kg}^{-1}$ According to the Huggins Equation			
283.1	0.02475	0.02459	0.02396	0.02462
288.1	0.02433	0.02395	0.02371	0.02419
293.1	0.02391	0.02379	0.02337	0.02354
298.1	0.02360	0.02304	0.02281	0.02290
303.1	0.02310	0.02243	0.02238	0.02238
308.1	0.02252	0.02210	0.02207	0.02207
313.1	0.02209	0.02179	0.02183	0.02185
	$[\eta]/\text{m}^3\cdot\text{kg}^{-1}$ According to the Kraemer Equation			
283.1	0.02482	0.02477	0.02417	0.02467
288.1	0.02439	0.02412	0.02391	0.02421
293.1	0.02396	0.02390	0.02359	0.02359
298.1	0.02363	0.02321	0.02307	0.02298
303.1	0.02313	0.02262	0.02265	0.02248
308.1	0.02256	0.02226	0.02231	0.02217
313.1	0.02212	0.02195	0.02206	0.02193

Table 3. Huggins Constant, k_H, and Kraemer Constant, k_K, of PVP with Uncertainty ± $1 \cdot 10^{-3}$ 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	0.446	0.475	0.498	0.423
288.1	0.428	0.475	0.498	0.384
293.1	0.409	0.430	0.518	0.436
298.1	0.395	0.489	0.554	0.502
303.1	0.398	0.525	0.580	0.558
308.1	0.407	0.503	0.578	0.560
313.1	0.397	0.513	0.565	0.543
	k_K			
283.1	−0.091	−0.084	−0.072	−0.103
288.1	−0.103	−0.084	−0.071	−0.129
293.1	−0.115	−0.108	−0.061	−0.094
298.1	−0.124	−0.074	−0.041	−0.046
303.1	−0.122	−0.052	−0.025	−0.006
308.1	−0.116	−0.064	−0.023	−0.005
313.1	−0.122	−0.056	−0.029	−0.015

The obtained intrinsic viscosities and Huggins constants are listed in Tables 2 and 3. 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 intrinsic viscosities and Kraemer constants are listed in Tables 2 and 3. Comparison of the results of Table 2 reveals that the obtained intrinsic viscosities from Huggins and Kraemer equations are comparable. The obtained intrinsic viscosities of PVP are decreased by increasing temperature and volume fraction of ethanol. Therefore, the hydrodynamic volume of the polymer coil is decreased by increasing temperature and volume fraction of ethanol. Nevertheless, the obtained intrinsic viscosities from Huggins reveals that the intrinsic viscosities of PVP in low temperatures slightly were increased by increasing volume fractions of ethanol from $\varphi_E = 0.15$ up to 0.20. The values of

Table 4. Expansion Factor, α, of PVP with Uncertainty ± $2\cdot10^{-3}$ in Various Mixtures of Water and Ethanol at Different Temperatures

	α			
T/K	$\varphi_E = 0.05$	$\varphi_E = 0.10$	$\varphi_E = 0.15$	$\varphi_E = 0.20$
283.1	2.487	2.482	2.461	2.483
288.1	2.474	2.460	2.452	2.469
293.1	2.459	2.455	2.440	2.446
298.1	2.449	2.429	2.421	2.424
303.1	2.431	2.407	2.406	2.406
308.1	2.411	2.395	2.394	2.394
313.1	2.395	2.384	2.386	2.386

Table 5. Heat of Dilution Parameter, κ, with Uncertainty ± $5\cdot10^{-4}$ in Various Mixtures of Water and Ethanol at Different Temperatures

	κ			
T/K	$\varphi_E = 0.05$	$\varphi_E = 0.10$	$\varphi_E = 0.15$	$\varphi_E = 0.20$
283.1	−0.1642	−0.1909	−0.1608	−0.2236
288.1	−0.1613	−0.1876	−0.1580	−0.2197
293.1	−0.1586	−0.1844	−0.1553	−0.2160
298.1	−0.1559	−0.1813	−0.1527	−0.2124
303.1	−0.1533	−0.1783	−0.1502	−0.2089
308.1	−0.1508	−0.1754	−0.1478	−0.2055
313.1	−0.1484	−0.1726	−0.1454	−0.2022

Table 6. Polymer−Solvent Interaction Parameter, χ, with Uncertainty ± $5\cdot10^{-4}$ in Various Mixtures of Water and Ethanol at Different Temperatures

	χ			
T/K	$\varphi_E = 0.05$	$\varphi_E = 0.10$	$\varphi_E = 0.15$	$\varphi_E = 0.20$
283.1	0.4145	0.4095	0.4065	0.3960
288.1	0.4174	0.4128	0.4093	0.3998
293.1	0.4201	0.4160	0.4120	0.4036
298.1	0.4228	0.4191	0.4146	0.4072
303.1	0.4254	0.4221	0.4171	0.4107
308.1	0.4279	0.4250	0.4196	0.4141
313.1	0.4303	0.4278	0.4219	0.4174

expansion factor were calculated using intrinsic viscosities which were obtained on the basis of the Huggins equation. The calculated expansion factors of PVP 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; therefore, the chain of PVP shrinks, and the end-to-end distance becomes smaller by increasing temperature. This behavior is maybe due to the effect of temperature on the interactions of segment−segment and segment−solvent. Perhaps the interaction of segment−segment is favored toward segment−solvent by increasing temperature; therefore, the hydrodynamic volume of the polymer coil becomes smaller by increasing temperature. For evaluation of 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 values of theta temperature for PVP in ethanol aqueous solutions with volume fractions of ethanol $\varphi_E = 0.05$, 0.10, 0.15, and 0.20 are (590, 538, 676, and 529) K, respectively. The obtained values of entropy of dilution parameter for PVP in mixtures of water and ethanol with the volume fractions of $\varphi_E = 0.05$, 0.10, 0.15, and 0.20 are −0.0787, −0.1004, −0.0674, and −0.1196, respectively. The obtained values of entropy of dilution parameter indicate that the entropy of dilution parameter is negative for PVP in all volume fractions of ethanol; that is, solvent molecules are ordered by PVP. However, the absolute value of entropy of dilution parameter is increased by increasing volume fractions of ethanol. This behavior is maybe due to the interaction of PVP−solvent. The interactions of water molecules with PVP were taking place alone with hydrophilic groups of PVP. However, the interactions of ethanol molecules with PVP were taking place with both hydrophilic and hydrophobic groups of PVP; therefore, the ethanol molecules rather than water are ordered by PVP. Nevertheless, the absolute value of entropy of dilution parameter showed a decrease in volume fractions of ethanol $\varphi_E = 0.15$. The volume fractions of ethanol $\varphi_E = 0.15$ nearly are correspondent to the mole fractions of ethanol 0.08. The mixing schemes of ethanol and water around the mole fractions of ethanol 0.08 seem to be qualitatively different which is clearly attributed to structural enhancement of the hydrogen bond network of water by ethanol, the so-called hydrophobic hydration.[17] Therefore, mixed water−ethanol with volume fractions of ethanol $\varphi_E = 0.15$ are less ordered by PVP. The values of the heat of dilution parameter for PVP in various volume fractions of ethanol and temperatures were calculated by eq 11, 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 PVP in all volume fractions of ethanol; that is, interactions of segment−solvent are favored toward segment−segment in PVP. However, the absolute value of heat of dilution parameter increased by increasing volume fractions of ethanol. This behavior is maybe due to the interaction of segment−ethanol being stronger than that of segment−water. Nevertheless, the absolute value of heat of dilution parameter showed a decrease in volume fractions of ethanol $\varphi_E = 0.15$ which is attributed to structural enhancement of the hydrogen bond network of water by ethanol. The values of the polymer−solvent interaction parameter are calculated by eq 12, and these values are listed in Table 6. The results of Table 6 indicate that the polymer−solvent interaction parameters for PVP 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 parameter, while a poor solvent has a high value of polymer−solvent interaction parameter; therefore, the results of Table 6 indicate that the quality of mixed water−ethanol was decreased for solutions of PVP by increasing temperature. The temperature dependency of χ is increased by increasing volume fractions of ethanol with the exception of $\varphi_E = 0.15$; therefore, temperature

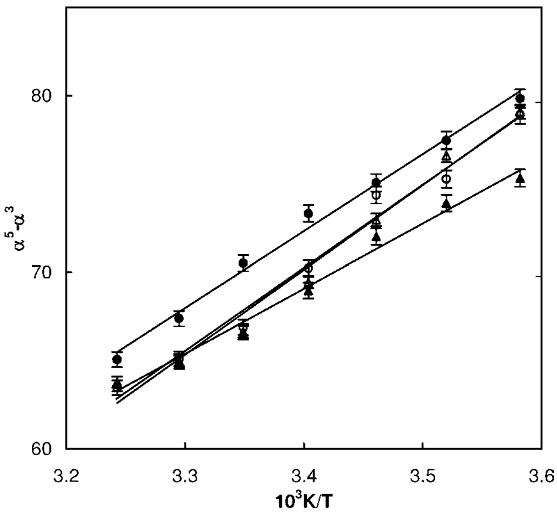

Figure 1. Plots of ($\alpha^5 - \alpha^3$) versus $1/T$ for PVP in water/ethanol with various volume fractions: ●, $\varphi_E = 0.05$; ○, $\varphi_E = 0.10$; ▲, $\varphi_E = 0.15$; Δ, $\varphi_E = 0.20$.

Table 7. Second Osmotic Virial Coefficient, *A*, with Uncertainty ± $1 \cdot 10^{-5}$ $m^3 \cdot mol \cdot kg^{-2}$ in Various Mixtures of Water and Ethanol at Different Temperatures

	$10^3 A/m^3 \cdot mol \cdot kg^{-2}$			
T/K	$\varphi_E = 0.05$	$\varphi_E = 0.10$	$\varphi_E = 0.15$	$\varphi_E = 0.20$
283.1	1.08	1.06	1.03	1.06
288.1	1.05	1.03	1.01	1.03
293.1	1.02	1.00	0.98	1.00
298.1	0.99	0.97	0.96	0.98
303.1	0.97	0.95	0.94	0.95
308.1	0.95	0.92	0.92	0.92
313.1	0.92	0.89	0.90	0.89

dependency of segment−segment and segment−solvent interactions is increased by increasing volume fractions of ethanol. Also, the results of Table 6 indicate that the quality of mixed water−ethanol was increased for solutions of PVP by increasing volume fractions of ethanol. The second osmotic virial coefficients were calculated by eq 13. The obtained second 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 was decreased for solutions of PVP by increasing temperature.

Conclusion

In this work, the effect of temperature and solvent composition on the intrinsic viscosity of poly(vinyl pyrrolidone) was investigated. The polymer solution thermodynamic parameters were evaluated by 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 poly(vinyl pyrrolidone) with increasing temperature.

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