Viscosity, Density, and Refractive Index of Poly(vinylpyrrolidone) + 1-Propanol and + 2-Propanol at 298.15 K

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The density, viscosity, and refractive index for the poly(vinylpyrrolidone) (PVP) + 1-propanol and poly(vinylpyrrolidone) + 2-propanol binary systems have been measured at 298.15 K. From the density data, the apparent specific volume of polymer and the partial specific volume of polymer and solvents have been calculated. The experimental viscosity and refractive index data have been successfully fit to a polynomial-type equation.

Introduction

Knowledge of the thermodynamic and transport properties of polymer solutions is important for practical purposes. Furthermore, the dependence of these properties on composition is of great interest from a theoretical standpoint because it may lead to a better understanding of the fundamental behavior of polymer solutions.

Thermodynamic and transport properties of aqueous poly(vinylpyrrolidone) (PVP) solution have been investigated in some detail by some research groups.[1−3] In this research work, for the first time, density, viscosity, and refractive index data of the PVP + 1-propanol and PVP + 2-propanol binary solutions have been measured at 298.15 K. The apparent specific volume of PVP and the partial specific volume of PVP and solvents were calculated using density data. The viscosity and refractive index data have been successfully fit to a polynomial-type equation.

Experimental Section

Materials. PVP (average molar mass = 10 000) was obtained from Sigma-Aldrich. 1-Propanol (GR, min 99.5 %) and 2-propanol (GR, min 99.5 %) were obtained from Merck and used without further purification.

Apparatus and Procedures. All solution density values were measured with a vibrating- tube densimeter (Mettler Toledo DE51), and refractive index values were measured with a refractometer (Mettler Toledo RE50) with proportional temperature control that kept the samples at working temperature with temperature stability of ± 0.01 K. The densimeter was calibrated with distilled water and dry air. The uncertainty in the density measurements was found to be $\pm\, 5 \cdot 10^{-5}$ $g \cdot cm^{-3}$. The refractometer was calibrated with distilled water, and the uncertainty of the instrument was found to be $\pm\, 3 \cdot 10^{-5}$ refractive index units. For each solution, density and refractive index were measured at least two times.

Viscosities were measured with an Ubbelohde-type viscometer. The temperature of the viscometer in the water bath was controlled to within ± 0.05 K. The flow time of investigated solution was measured with an accuracy better than 0.1 s. For each solution, the flow time was measured at least three times.

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Table 1. Densities (ρ) and Polymer Apparent Specific Volumes ($v_{2\phi}$) of PVP + 1-Propanol and PVP + 2-Propanol Binary Systems as a Function of the Polymer Mass Fraction (w) at 298.15 K

	PVP + 1-propanol		PVP + 2-propanol	
w	ρ/g·cm^{-3}	$v_{2\phi}$/cm^3·g^{-1}	ρ/g·cm^{-3}	$v_{2\phi}$/cm^3·g^{-1}
0.000	0.79975		0.78550	
0.005	0.80128	0.7728	0.78598	2.1448
0.010	0.80281	0.7737	0.78671	1.4337
0.020	0.80589	0.7741	0.78876	1.0905
0.030	0.80888	0.7799	0.79128	0.9631
0.040	0.81221	0.7708	0.79445	0.9145
0.050	0.81541	0.7701	0.79772	0.8830
0.060	0.81843	0.7747	0.80096	0.8635
0.070	0.82166	0.7741	0.80362	0.8630
0.080	0.82439	0.7733	0.80731	0.8432
0.090	0.82814	0.7741	0.81081	0.8315
0.100	0.83133	0.7754	0.81389	0.8290
0.125	0.83217	0.7836	0.82258	0.8140
0.150	0.83416	0.7817	0.83122	0.8063
0.175	0.85704	0.7728	0.84006	0.8006
0.200	0.86565	0.7744	0.84898	0.7971
0.250	0.88219	0.7830	0.86733	0.7926
0.300	0.90071	0.7832	0.88675	0.7885
0.350	0.91896	0.7870	0.90655	0.7874
0.400	0.94110	0.7809	0.92617	0.7897
0.450	0.95752	0.7926	0.94302	0.8005

The uncertainty for the viscosity measurements was estimated to be ± 0.5 %. Two stock solutions of PVP + 1-propanol and + 2-propanol were gravimetrically prepared with an analytical balance with an uncertainty of $\pm\, 1 \cdot 10^{-4}$ g, and all solutions were made from the stock solutions.

Results and Discussion

The densities, viscosities, and refractive indices of PVP + 1-propanol and PVP + 2-propanol binary solutions have been measured at 298.15 K and reported in Tables 1 and 2. We computed the apparent specific volume of the polymer, $v_{2\phi}$, from the density of the solution by using the following equation

$$v_{2\phi} = \frac{1}{w}\left(\frac{1}{\rho} - \frac{1-w}{\rho_1}\right) \tag{1}$$

where ρ and ρ_1 are, respectively, the density of the solution and that of pure alcohol and w is the mass fraction of the polymer. The calculated values of $v_{2\phi}$ have been given in Table

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Table 2. Viscosities (η) and Refractive Indices (n_D) of PVP + 1-Propanol and PVP + 2-Propanol Binary Systems as a Function of the Polymer Mass Fraction (w) at 298.15 K

	PVP + 1-propanol		PVP + 2-propanol	
w	η/mPa·s	n_D	η/mPa·s	n_D
0.000	1.945	1.38311	2.038	1.37501
0.005	2.827	1.38362	2.932	1.37560
0.010	2.924	1.38418	3.084	1.37624
0.020	3.149	1.38507	3.477	1.37751
0.030	3.431	1.38624	3.8183	1.37857
0.040	3.742	1.38738	4.145	1.37994
0.050	3.962	1.38892	4.437	1.38116
0.060	4.485	1.39003	4.902	1.38242
0.070	4.794	1.39111	5.211	1.38344
0.080	5.119	1.39229	5.788	1.38478
0.090	5.774	1.39367	6.566	1.38613
0.100	6.344	1.39449	7.180	1.38732
0.125	7.884	1.39736	9.576	1.39052
0.150	10.06	1.40048	12.242	1.39378
0.175	11.168	1.40314	14.690	1.39709
0.200	14.724	1.40645	19.578	1.40049
0.250	24.717	1.41280	29.240	1.40745
0.300	38.440	1.41962	45.373	1.41488
0.350	57.905	1.42725	74.020	1.42237
0.400	84.504	1.43480	116.183	1.43018
0.450	113.914	1.44334	163.360	1.43597

Table 3. Apparent Specific Volume of the Polymer at Infinite Dilution ($v_{2\phi}^{\infty}$) and Empirical Parameters of Equation *2* with Average Relative Deviation (AARD)

system	$v_{2\phi}^{\infty}$	b_v	b_{vv}	AARD[a]
PVP + 1-propanol	0.7733	0.0189	0.0383	0.004
PVP + 2-propanol	1.0245	− 2.0047	3.5757	0.03

[a] AARD = $1/[N\sum (|v_{2\phi}^{\text{exptl}} - v_{2\phi}^{\text{theor}}|/v_{2\phi}^{\text{exptl}})]$.

2. In Figure 1, the composition dependence of $v_{2\phi}$ has been shown. The $v_{2\phi}$ values were fit to the following equation

$$v_{2\phi} = v_{2\phi}^{\infty} + b_v w + b_{vv} w^2 \quad (2)$$

where $v_{2\phi}^{\infty}$ is the apparent specific volume of the polymer at infinite dilution and b_v and b_{vv} are the empirical parameters that depend on solute, solvent, and $m_{w2,}$ the weight molality of polymer (grams of polymer per grams of alcohol). The coefficients b_v and b_{vv} of eq 2 are obtained and reported in Table 3. Volumetric properties of PVP in water have been previously investigated by Sadeghi et al.[2] in detail. The $v_{2\phi}$ values of the PVP + H_2O system, obtained from their data,[2] are compared with $v_{2\phi}$ values of PVP + 1-propanol and PVP + 2-propanol binary systems calculated in this work and shown in Figure 1.

The partial specific volume of the polymer, v_2, is related to its apparent specific volume by the expression[4]

$$v_2 = v_{2\phi} + w\left(\frac{\partial v_{2\phi}}{\partial w}\right)_{T,P} \quad (3)$$

By considering eq 2 for $v_{2\phi}$, we have

$$v_2 = v_{2\phi}^{\infty} + 2b_v w + 3b_{vv} w^2 \quad (4)$$

The partial specific volume of water, v_1, can be obtained from

$$v_1 = v_1^{\infty} - b_v w^2 - 2b_{vv} w^3 \quad (5)$$

where $v_1^{\infty} = 1/\rho_1$. In Figures 2 and 3, the concentration dependence of the calculated values of v_1 and v_2 are shown. As can be seen from Figures 2 and 3, for 1-propanol and H_2O systems, the partial specific volume of the polymer and solvent do not show much variation with the concentration of PVP, but in the case of 2-propanol, this variation is greater.

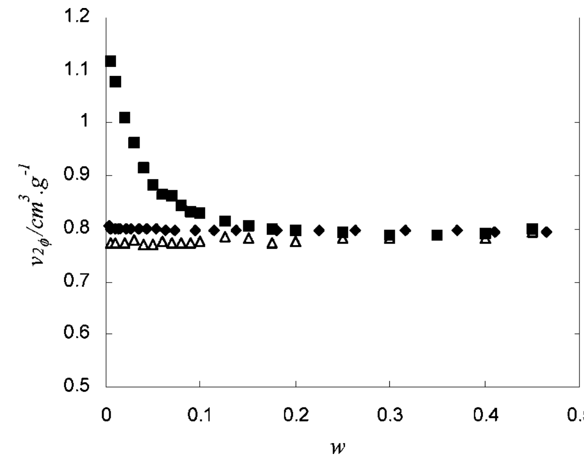

Figure 1. Plot of apparent specific volume of PVP, $v_{2\phi}$, against mass fraction of polymer for different solvents: △, 1-propanol; ■, 2-propanol; ◆, H_2O.

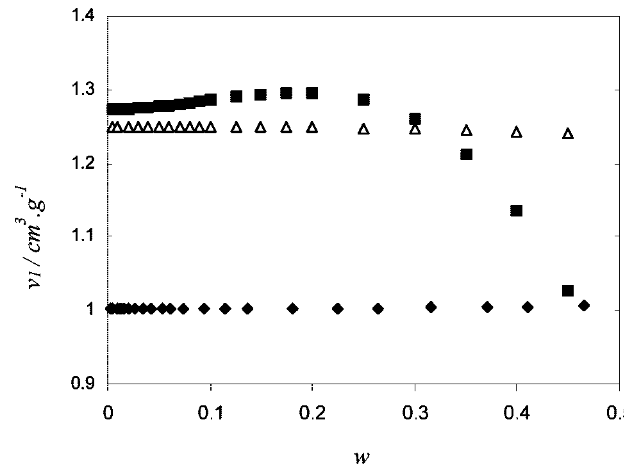

Figure 2. Plot of calculated partial specific volume of the solvent, v_1, against mass fraction of polymer for different solvents: △, 1-propanol; ■, 2-propanol; ◆, H_2O.

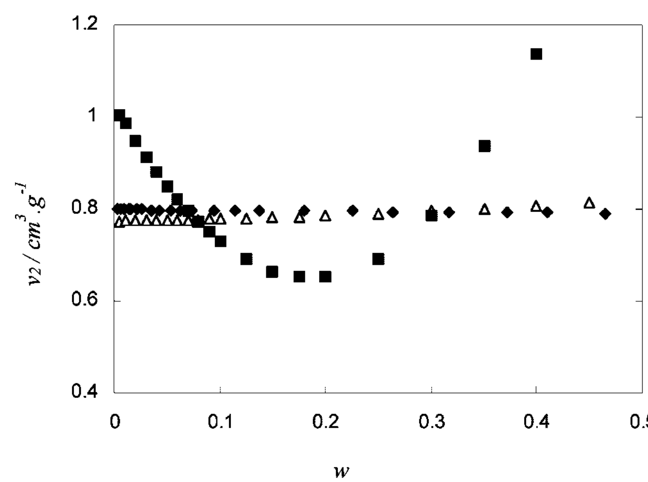

Figure 3. Plot of calculated partial specific volume of PVP, v_2, against mass fraction of polymer for different solvents: △, 1-propanol; ■, 2-propanol; ◆, H_2O.

The experimental refractive index and viscosity of the PVP + 1-propanol and PVP + 1-propanol solutions were successfully fit to a polynomial-type equation

Table 4. Fitting Parameters of Equation *6* Together with Their Absolute Average Relative Deviation (AARD)

	system	a_0	a_1	a_2	a_3	AARD[a]
η	PVP + 1-propanol	1.945	39.623	− 114.82	1301.30	0.5
	PVP + 2-propanol	2.038	81.089	− 521.90	2538.50	0.8
n_D	PVP + 1-propanol	1.3831	0.1054	0.0606		0.0003
	PVP + 2-propanol	1.3750	0.1206	0.0379		0.0002

[a] AARD = $1/[N\sum (|M^{\text{exptl}} - M^{\text{theor}}|/M^{\text{exptl}})]$, where M is η or n_D.

$$\eta \text{ or } n_D = a_0 + a_1 w + a_2 w^2 + ... \tag{6}$$

where w is the mass fraction of polymer and a_i is curve-fit coefficient. Fitting parameters of this equation for refractive index and viscosity together with their standard deviations are given in Table 4.

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