Volumetric, Compressibility, and Viscometric Measurements of Binary Mixtures of Poly(vinylpyrrolidone) + Water, + Methanol, + Ethanol, + Acetonitrile, + 1-Propanol, + 2-Propanol, and + 1-Butanol

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The apparent specific volumes and isentropic compressibilities of poly(vinylpyrrolidone) (PVP) in water, methanol, ethanol, acetonitrile, 1-propanol, 2-propanol, and 1-butanol have been obtained at the (288.15 to 313.15) K temperature range at 5 K intervals at atmospheric pressure from measurements of density and speed of sound. The infinite dilution apparent specific volume and isentropic compressibility values of PVP in the investigated solvents have been obtained, and their variations with temperature and type of solvents have also been obtained. The results have been interpreted in terms of the interactions between different solvents and the polymer. In the second part of this work, viscosity measurements have been carried out on the all mentioned solutions at $T =$ (293.15, 298.15, 303.15, 308.15, and 313.15) K at atmospheric pressure. The variations of viscosity with the concentration of polymer, temperature, and type of solvent have been determined. The results have been correlated successfully with the segment-based Eyring−Wilson and nonrandom two-liquid (NRTL) viscosity models. It was found that the Wilson model produces better results than the NRTL model.

Introduction

Poly(vinylpyrrolidone) (PVP) is a well-known water-soluble polymer, and it is subject to interaction with aqueous and nonaqueous solvents. Thermodynamic and transport properties such as volumetric, acoustical, and viscometric properties of polymer solutions have been proven to be a very useful tool for understanding solute−solvent and solute−solute interactions in these solutions. Although PVP is a very important polymer in respect to its use in biotechnology, information on the thermodynamics properties of aqueous or nonaqueous solutions of this polymer is relatively scarce in the literature.[1−7] Regarding the thermodynamic properties of nonaqueous solutions of PVP, recently Zafarani-Moattar and Khoshsima[7] measured the density and viscosity of binary PVP + methanol, + ethanol, and + 1-propanol solutions at $T =$ (298.15, 308.15, and 318.15) K. In fact, as far as we know, this is the only report on the volumetric and viscometric properties of nonaqueous solutions of PVP. However, the density data reported by Zafarani-Moattar and Khoshsima[7] have been measured using a single-arm capillary pycnometer having a bulb volume of approximately $1 \cdot 10^{-5}$ m^3 with a low uncertainty of $\pm 1 \cdot 10^{-1}$ kg·m^{-3}. In the present study, precise density, speed of sound, and viscosity measurements have been carried out on the binary solutions of PVP + water, + methanol, + ethanol, + acetonitrile, + 1-propanol, + 2-propanol, and + 1-butanol at $T =$ (288.15, 293.15, 298.15, 303.15, 308.15, and 313.15) K at atmospheric pressure. From these experimental data, the infinite dilution apparent specific volume and isentropic compressibility of PVP in the investigated solvents as well as their variations with temperature and type of solvents have been determined.

Experimental Procedure

Methanol ($w > 0.999$, CAS No. 67-56-1), ethanol ($w > 0.999$, CAS No. 64-17-5), acetonitrile ($w > 0.999$, CAS No. 75-05-8), 1-propanol ($w > 0.998$, CAS No. 71-23-8), 2-propanol ($w > 0.995$, CAS No. 67-63-0), 1-butanol ($w > 0.990$, CAS No. 71-36-3), and PVP (average molar mass = 10000, CAS No. 9003-39-8) were obtained from Merck and were used without further purification. PVP has been characterized by the manufacturer as polyvidon 25 with lot number k38734343 831. Double-distilled and deionized water was used.

All of the solutions were prepared by mass on a Sartorius CP124S balance precise to within $\pm 1 \cdot 10^{-7}$ kg. The density and speed of sound of the mixtures were measured at different temperatures with a digital vibrating-tube analyzer (Anton Paar DSA 5000, Austria) with a proportional temperature control that kept the samples at working temperature within $\pm 10^{-3}$ K. The apparatus was calibrated with double-distilled deionized and degassed water and dry air at atmospheric pressure according to the instrument catalog. Densities and speed of sounds can be measured to $\pm 10^{-3}$ kg·m^{-3} and $\pm 10^{-2}$ m·s^{-1}, respectively, under the most favorable conditions. The uncertainties of density and speed of sound measurements were better than $\pm 5 \cdot 10^{-3}$ kg·m^{-3} and $\pm 2 \cdot 10^{-1}$ m·s^{-1}, respectively.

Viscosities were measured with an Ostwald-type viscometer. It was assumed that the dynamic viscosity η was related to the time of flow according to

$$\eta = Ldt - \frac{Nd}{t} \qquad (1)$$

where t is the flow time, d is the density of the solution, and L and N are constants characteristic of the viscometer. The viscometer constants L and N were determined by a least-squares fit to eq 1 of the literature data for the viscosity of water[8] and 2-propanol[9] at the respective temperature. The temperature of the water bath was maintained at ± 0.02 K. The flow time of investigated solutions was measured with an accuracy better than 0.05 s. For each solution the flow time was measured at least three times. The uncertainty for the dynamic viscosity determination was estimated to be ± 0.1 %.

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Table 1. Comparison of the Density, d/(kg·m^{-3}), Speed of Sound, u/(m·s^{-1}), and Viscosity, η/(Pa·s) of Pure Solvents Obtained in This Study with Literature Values at T = 298.15 K

	d/(kg·m^{-3})			u/(m·s^{-1})			10^3 η/(Pa·s)		
solvent	this work	literature values		this work	literature values		this work	literature values	
methanol	786.520	786.6[7] 786.37[11] 786.693[19] 786.54[25] 786.548[23]	786.63[10] 786.6[14] 786.531[24] 786.56[31]	1102.13	1108.30[19] 1102.68[24] 1101.9[31]	1102.62[23] 1101.9[25]	0.549	0.542[7] 0.5513[11] 0.545[15]	0.553[10] 0.553[14]
ethanol	785.096	784.9[7] 784.93[11] 785.0[14]	785.25[10] 785.10[13] 785.085[19]	1142.92	1143.49[13] 1143.39[32] 1143.3[38]	1143.10[19] 1144.7[37]	1.093	1.093[7] 1.0826[11] 1.105[14]	1.09[10] 1.0930[13]
acetonitrile	776.744	776.533[16] 776.609[18]	776.67[17] 776.533[24]	1278.60	1278.62[16] 1278.62[24] 1279.18[32]	1278.77[18] 1280.8[26]	0.354	0.3696[27] 0.3369[29]	0.341[28] 0.342[30]
1-propanol	799.506	799.3[7] 799.60[11] 799.527[19] 799.58[34]	799.54[10] 799.5[14] 799.666[23]	1205.35	1205.76[19] 1206.0[36]	1206.47[23] 1208.9[37]	1.947	1.803[7] 1.9430[11] 1.915[34]	1.95[10] 1.970[14]
2-propanol	780.856	780.88[13] 780.824[19] 780.804[32]	780.9[14] 781.06[20] 780.87[34]	1138.47	1138.94[13] 1142[20]	1138.87[19] 1139.10[32]	2.072	2.089[13] 2.098[20]	2.098[14] 2.0436[11]
1-butanol	805.845	805.84[12] 805.9[14] 805.73[21]	805.75[11,34] 805.778[19] 806.06[22]	1239.77	1240.16[19] 1240.0[34] 1239.7[37]	1240.3[33] 1240.2[35] 1239.39[39]	2.569	2.620[14] 2.5609[21] 2.60[39]	2.571[15,34] 2.619[22]

Density, speed of sound, and viscosity values of the pure solvents are given in Table 1 at 298.15 K and compared with the literature values.[7,10−39]

Results and Discussion

Table 2 reports the measured densities (d) and speed of sounds (u), and Table 3 reports the measured viscosities for the investigated binary solutions determined at different temperatures. In these tables, m_{wp} is the weight molality of polymer (kg polymer per kg of solvent) which has an uncertainty better than $\pm\ 3 \cdot 10^{-4}$.

The apparent specific volume, ϕ_V, and apparent specific isentropic compressibility, ϕ_K, of PVP were computed from the density and speed of sound experimental data according to the following equations:

$$\phi_V = \frac{1 + m_{\mathrm{wp}}}{m_{\mathrm{wp}} d} - \frac{1}{m_{\mathrm{wp}} d_0} \qquad (2)$$

$$\phi_K = \frac{(1 + m_{\mathrm{wp}})\kappa_{\mathrm{s}}}{d m_{\mathrm{wp}}} - \frac{\kappa_{\mathrm{s0}}}{d_0 m_{\mathrm{wp}}} \qquad (3)$$

where d_0 and d are the densities of the solvent and the solution, respectively, and κ_{s0} and κ_{s} are isentropic compressibilities of solvent and solution, respectively. In Figure 1, the measured apparent specific volume of PVP in different solvents investigated in this work are shown at T = 298.15 K. To calculate the values of the standard or infinite dilution partial specific volume, ϕ_V^0, and isentropic compressibility, ϕ_K^0, the values of ϕ_V and ϕ_K at each temperature were fitted by a least-squares method to the following equations:[40]

$$\phi_V = \phi_V^0 + b_V m_{\mathrm{wp}}^{0.5} + b_{VV} m_{\mathrm{wp}}^{1.5} \qquad (4)$$

$$\phi_K = \phi_K^0 + b_K m_{\mathrm{wp}}^{0.5} + b_{KK} m_{\mathrm{wp}}^{1.5} \qquad (5)$$

where b_V, b_{VV}, b_K, and b_{KK} are empirical parameters which depend on solute, solvent, and temperature. The obtained values of ϕ_V^0 and ϕ_K^0 along with the values of b_V, b_{VV}, b_K, and b_{KK} at different temperatures calculated from the fitting of the experimental data to eqs 4 and 5 are presented in Tables 4 and 5, respectively, and the corresponding deviations are given in Table 6. In Table 7, the obtained ϕ_V^0 for PVP in water, methanol, ethanol, and 1-propanol measured in this work were compared with the values reported in the literature. A similar comparison for the other investigated systems cannot be made at this time since these data are lacking in the literature. As can be seen, although our results are in good agreement with ref 3, our results do not agree well with ref 7.

As can be seen from Table 4 and Figure 2, at each temperature, the obtained values of ϕ_V^0 of PVP in the investigated solvents follow the order: methanol < ethanol < 2-propanol < 1-propanol < butanol < water < acetonitrile. The infinite dilution apparent specific volume can be expressed as the sum of two contributions:[41]

$$\phi_V^0 = \phi_V^0(\mathrm{int}) + \phi_V^0(\mathrm{elect}) \qquad (6)$$

where $\phi_V^0(\mathrm{int})$ is the intrinsic volume of the nonsolvated solute molecule and $\phi_V^0(\mathrm{elect})$ is the electrostriction apparent specific volume due to the solvation of the solute (i.e., the volume change undergone by the solvent molecules in the solvation process). The $\phi_V^0(\mathrm{int})$ is made up of two terms, the van der Waals volume and the volume change due to packing effects. The smaller solvent molecules have a larger packing effect and therefore have a smaller $\phi_V^0(\mathrm{int})$. On the other hand, if PVP manifests a structure-making effect for solvent, the second contribution will be positive, whereas it is negative in the case of structure-breaking. Therefore, we may conclude that the sequence of ϕ_V^0 of investigated solutions reflects the balance between the packing and structure-breaking (solvent−solute interactions) effects. From the molar volume of the pure solvents, we can say that the packing effect for the investigated systems follow the order: water > methanol > ethanol > acetonitrile > 1-propanol > 2-propanol > 1-butanol. Therefore, from the obtained ϕ_V^0 data and this trend for the packing effect, we only can conclude that the structure-breaking effect of PVP on the studied solvents follows the order: water (or acetonitrile) < 1-propanol < 2-propanol. Vapor pressure of pure solvents, p_0, for methanol, acetonitrile, ethanol, 2-propanol, water, and 1-butanol at T =

Table 2. Experimental Density $d/(\mathrm{kg \cdot m^{-3}})$ and Speed of Sound $u/(\mathrm{m \cdot s^{-1}})$ for Solutions of PVP in Different Solvents as a Function of Polymer Weight Molality, m_{wp} (kg Polymer per kg of Solvent) at Different Temperatures T

	T/K = 288.15		T/K = 293.15		T/K = 298.15		T/K = 303.15		T/K = 308.15		T/K = 313.15	
m_{wp}	d	u	d	u	d	u	d	u	d	u	d	u
PVP + Water												
0.0000	999.699	1447.59	999.099	1466.25	998.203	1482.66	997.043	1497.00	995.645	1509.44	994.029	1520.12
0.0060	1000.358	1469.19	999.446	1485.13	998.271	1499.24	996.862	1511.50	995.235	1522.04	993.409	1530.99
0.0090	1000.975	1470.53	1000.056	1486.41	998.875	1500.44	997.459	1512.62	995.828	1523.08	993.994	1532.00
0.0111	1001.410	1471.37	1000.486	1487.17	999.301	1501.15	997.882	1513.28	996.244	1523.74	994.410	1532.60
0.0156	1002.334	1473.49	1001.402	1489.17	1000.206	1503.03	998.779	1515.02	997.136	1525.38	995.293	1534.16
0.0541	1009.954	1490.46	1008.940	1505.20	1007.665	1518.14	1006.166	1529.30	1004.458	1538.80	1002.553	1546.77
0.0666	1012.338	1495.91	1011.290	1510.30	1009.992	1522.93	1008.469	1533.82	1006.740	1543.07	1004.818	1550.77
0.1291	1023.687	1523.07	1022.505	1535.81	1021.087	1546.87	1019.454	1556.29	1017.624	1564.17	1015.611	1570.57
0.1393	1025.465	1527.25	1024.263	1539.72	1022.826	1550.54	1021.176	1559.76	1019.329	1567.43	1017.301	1573.64
0.1393	1025.452	1527.19	1024.249	1539.67	1022.813	1550.50	1021.162	1559.72	1019.317	1567.38	1017.288	1573.58
0.2174	1038.117	1559.43	1036.759	1569.85	1035.182	1578.74	1033.404	1586.14	1031.442	1592.12	1029.304	1596.76
0.2712	1046.075	1581.04	1044.635	1590.03	1043.006	1597.63	1041.113	1603.81	1039.054	1608.62	1036.845	1612.18
0.3505	1056.950	1610.53	1055.325	1617.56	1053.528	1623.28	1051.553	1627.73	1049.407	1630.96	1047.102	1633.01
0.4176	1065.434	1636.10	1063.755	1641.35	1061.863	1645.43	1059.790	1648.36	1057.540	1650.17	1055.124	1650.92
0.4199	1065.780	1636.26	1064.069	1641.49	1062.163	1645.56	1060.093	1648.48	1057.855	1650.28	1055.469	1651.02
PVP + Methanol												
0.0000	795.920	1135.10	791.230	1118.64	786.520	1102.13	781.793	1085.75	777.042	1069.51	772.265	1053.39
0.0204	802.290	1140.61	797.611	1124.10	792.914	1107.60	788.202	1091.19	783.466	1074.93	778.700	1058.78
0.0309	805.487	1142.97	800.816	1126.49	796.124	1109.99	791.418	1093.60	786.689	1077.37	781.929	1061.20
0.0517	811.721	1148.49	807.057	1131.97	802.380	1115.41	797.687	1099.01	792.973	1082.73	788.230	1066.57
0.0794	819.788	1154.99	815.145	1138.51	810.485	1122.00	805.809	1105.64	801.110	1089.38	796.385	1073.21
0.1752	845.652	1180.52	841.076	1164.08	836.482	1147.60	831.872	1131.28	827.242	1115.04	822.585	1098.89
0.2494	863.812	1200.76	859.280	1184.39	854.730	1167.94	850.167	1151.62	845.581	1135.40	840.973	1119.26
0.3318	882.270	1220.42	877.791	1204.13	873.298	1187.70	868.790	1171.35	864.258	1155.09	859.711	1139.00
0.4284	901.984	1245.38	897.570	1229.02	893.137	1212.60	888.693	1196.31	884.228	1180.17	879.742	1164.07
PVP + Ethanol												
0.0000	793.651	1177.03	789.386	1159.98	785.096	1142.92	780.779	1125.97	776.431	1109.16	772.044	1092.42
0.0202	799.859	1182.35	795.600	1165.34	791.318	1148.34	787.004	1131.37	782.661	1114.58	778.278	1097.83
0.0807	817.456	1197.88	813.217	1180.96	808.949	1163.96	804.655	1147.07	800.331	1130.33	795.965	1113.56
0.1028	823.494	1203.29	819.260	1186.49	814.997	1169.51	810.709	1152.66	806.391	1135.86	802.033	1119.13
0.1759	842.450	1221.95	838.242	1205.10	834.004	1188.17	829.744	1171.41	825.451	1154.68	821.118	1137.93
0.2493	859.926	1239.95	855.745	1223.20	851.539	1206.35	847.304	1189.63	843.038	1172.92	838.736	1156.25
0.3329	877.753	1258.95	873.601	1242.13	869.429	1225.32	865.229	1208.57	860.990	1191.93	856.736	1175.32
0.4214	895.178	1279.55	891.074	1262.85	886.940	1246.08	882.781	1229.46	878.588	1212.83	874.363	1196.28
PVP + Acetonitrile												
0.0000	787.516	1318.78	782.143	1298.80	776.744	1278.60	771.318	1258.48	765.860	1238.33	760.370	1218.20
0.0504	801.933	1322.21	796.600	1302.27	791.238	1282.13	785.849	1262.04	780.431	1241.94	774.979	1221.83
0.0621	805.213	1323.13	799.888	1303.14	794.534	1283.02	789.153	1262.93	783.744	1242.83	778.304	1222.78
0.0743	808.590	1323.95	803.276	1304.03	797.930	1283.90	792.561	1263.84	787.162	1243.77	781.729	1223.70
0.0929	813.604	1325.33	808.303	1305.45	802.974	1285.37	797.619	1265.35	792.234	1245.31	786.817	1225.28
0.1058	817.032	1326.39	811.744	1306.48	806.422	1286.40	801.077	1266.38	795.703	1246.38	790.295	1226.36
0.1425	826.486	1329.26	821.227	1309.46	815.935	1289.47	810.62	1269.53	805.273	1249.54	799.898	1229.63
0.1742	834.371	1331.98	829.138	1312.24	823.874	1292.30	818.584	1272.41	813.270	1252.51	807.917	1232.58
0.2056	841.788	1334.68	836.578	1315.01	831.340	1295.16	826.074	1275.37	820.780	1255.52	815.455	1235.68
0.2849	859.694	1342.70	854.548	1323.11	849.372	1303.31	844.171	1283.58	838.944	1263.84	833.685	1244.06
0.3292	868.931	1347.40	863.820	1327.87	858.675	1308.14	853.509	1288.48	848.315	1268.86	843.096	1249.19
0.4167	886.106	1357.73	881.060	1338.20	875.984	1318.58	870.885	1299.01	865.762	1279.49	860.609	1259.94
PVP + 1-Propanol												
0.0000	807.494	1239.72	803.516	1222.59	799.506	1205.35	795.476	1188.38	791.406	1171.47	787.296	1154.64
0.0101	810.507	1242.16	806.529	1225.09	802.523	1207.96	798.487	1190.94	794.416	1174.02	790.304	1157.17
0.0204	813.527	1244.62	809.547	1227.52	805.539	1210.38	801.503	1193.37	797.430	1176.43	793.319	1159.59
0.0526	822.691	1252.23	818.709	1235.12	814.701	1217.97	810.663	1200.94	806.592	1184.04	802.480	1167.16
0.0809	830.380	1258.66	826.402	1241.60	822.393	1224.47	818.357	1207.49	814.288	1190.56	810.178	1173.69
0.1111	838.315	1265.61	834.335	1248.54	830.332	1231.46	826.298	1214.47	822.234	1197.60	818.126	1180.72
0.1376	845.074	1271.54	841.102	1254.51	837.105	1237.40	833.076	1220.41	829.015	1203.50	824.917	1186.66
0.2041	861.039	1286.29	857.085	1269.29	853.098	1252.23	849.084	1235.29	845.039	1218.44	840.955	1201.61
0.2494	871.187	1297.40	867.242	1280.49	863.264	1263.50	859.258	1246.62	855.221	1229.83	851.144	1213.06
0.3262	887.233	1313.25	883.321	1296.40	879.367	1279.45	875.387	1262.60	871.377	1245.84	867.328	1229.12
0.4276	906.100	1333.44	902.236	1316.55	898.345	1299.92	894.413	1282.20	890.441	1266.08	886.431	1249.42
PVP + 2-Propanol												
0.0000	789.196	1173.20	785.060	1155.90	780.856	1138.47	776.587	1121.01	772.238	1103.51	767.802	1085.92
0.0204	795.357	1178.74	791.216	1161.42	787.013	1143.92	782.739	1126.44	778.393	1108.94	773.958	1091.31
0.0296	798.091	1181.10	793.949	1163.77	789.745	1146.27	785.474	1128.80	781.127	1111.29	776.695	1093.66
0.0417	801.580	1184.29	797.437	1166.98	793.231	1149.47	788.960	1131.99	784.614	1114.46	780.185	1096.82
0.0639	807.901	1189.98	803.757	1172.67	799.553	1155.15	795.286	1137.68	790.946	1120.11	786.522	1102.45
0.0811	812.657	1194.19	808.517	1176.88	804.317	1159.37	800.055	1141.88	795.720	1124.32	791.305	1106.70
0.0929	815.890	1197.51	811.753	1180.21	807.550	1162.70	803.288	1145.20	798.953	1127.65	794.539	1110.00
0.1109	820.701	1201.93	816.566	1184.62	812.367	1167.12	808.111	1149.65	803.783	1132.07	799.376	1114.42
0.1762	837.260	1217.84	833.145	1200.56	828.968	1183.09	824.734	1165.62	820.436	1148.14	816.063	1130.54
0.2498	854.507	1235.66	850.422	1218.40	846.277	1200.98	842.074	1183.58	837.812	1166.12	833.480	1148.58
0.3328	872.214	1255.72	868.172	1238.48	864.064	1221.11	859.901	1203.73	855.677	1186.34	851.384	1168.86
0.4094	887.170	1273.11	883.177	1255.92	879.133	1238.57	875.025	1221.27	870.851	1203.97	866.605	1186.56

Table 2. Continued

	T/K = 288.15		T/K = 293.15		T/K = 298.15		T/K = 303.15		T/K = 308.15		T/K = 313.15	
m_{wp}	d	u	d	u	d	u	d	u	d	u	d	u
PVP + 1-Butanol												
0.0000	813.452	1273.55	809.660	1256.65	805.845	1239.77	802.004	1222.98	798.133	1206.32	794.222	1189.70
0.0081	815.795	1275.29	812.002	1258.46	808.182	1241.56	804.338	1224.78	800.462	1208.12	796.550	1191.52
0.0204	819.311	1277.98	815.515	1261.15	811.692	1244.26	807.845	1227.50	803.966	1210.82	800.051	1194.19
0.0307	822.220	1280.28	818.418	1263.41	814.594	1246.52	810.743	1229.72	806.861	1213.02	802.944	1196.39
0.0520	828.102	1284.37	824.304	1267.57	820.477	1250.68	816.627	1233.95	812.747	1217.25	808.828	1200.61
0.0809	835.812	1290.24	832.013	1273.45	828.186	1256.58	824.335	1239.83	820.455	1223.15	816.535	1206.53
0.1108	843.602	1296.06	839.806	1279.29	835.982	1262.44	832.135	1245.72	828.260	1229.07	824.347	1212.48
0.1382	850.406	1301.56	846.613	1284.79	842.791	1267.97	838.946	1251.28	835.074	1234.66	831.166	1218.09
0.1727	858.672	1308.50	854.885	1291.82	851.067	1275.04	847.226	1258.33	843.355	1241.72	839.452	1225.16
0.2036	865.698	1314.70	861.908	1298.02	858.088	1281.27	854.250	1264.59	850.380	1248.03	846.477	1231.50
0.3290	891.986	1339.01	888.247	1322.41	884.467	1305.68	880.663	1289.10	876.831	1272.62	872.961	1256.18
0.3713	899.907	1347.05	896.200	1330.45	892.442	1313.79	888.651	1297.26	884.830	1280.81	880.973	1264.38
0.4254	909.402	1357.07	905.621	1340.50	901.862	1323.86	898.107	1307.34	894.310	1290.89	890.477	1274.53
0.4432	912.297	1361.42	908.504	1344.88	904.739	1328.25	900.971	1311.73	897.163	1295.37	893.312	1279.03

298.15 K are (16.958, 11.983, 7.870, 5.777, 3.169, and 0.824) kPa, respectively. From the plots of vapor pressure depression (Figure 3) it would be expected that the PVP−solvent interaction follows the sequence: water < 1-butanol < acetonitrile < 2-propanol < ethanol < methanol.

The temperature dependence of ϕ_V^0 was fitted by a least-squares method to the following equation:[42]

$$\phi_V^0 = a + bT^{0.5} + c\ln(T) \qquad (7)$$

and from which the infinite dilution apparent specific expansibilities, $\phi_E^0 = (\partial\phi_V^0/\partial T)_P$, were obtained, which are shown in Figure 4. The values of obtained parameters a, b, and c are given in Table 8.

In Figure 5, the values of κ_s for solutions of PVP in water and in 2-propanol have been shown at different temperatures. Figure 6 shows that the values of κ_s of pure nonaqueous solvents increase with the increase in temperature. A similar behavior has also been observed for pure polymers.[43,44] On the other hand, the compressibility of pure water decreases slightly with temperature to a minimum κ_s value near 337.15 K and then increases gradually. The isentropic compressibility of a solution can be taken as the sum of two contributions, κ_s(solvent intrinsic) and κ_s(solute intrinsic). For the concentration range investigated in this study (low concentrations) the κ_s(solvent intrinsic) is the

Table 3. Experimental Viscosity, $10^3\ \eta/(\mathrm{Pa\cdot s})$, for Solutions of PVP in Different Solvents as a Function of Polymer Weight Molality, m_{wp} (kg Polymer per kg of Solvent), at Different Temperatures T

m_{wp}	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	m_{wp}	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
PVP + Water											
0.0000	1.003	0.890	0.797	0.719	0.653	0.0494	2.249	1.923	1.691	1.503	1.357
0.0015	1.014	0.904	0.811	0.724	0.661	0.0669	2.821	2.452	2.146	1.890	1.706
0.0030	1.038	0.924	0.828	0.746	0.677	0.0785	3.264	2.820	2.460	2.177	1.942
0.0088	1.159	1.023	0.925	0.818	0.744	0.0939	3.983	3.408	2.974	2.610	2.326
0.0156	1.295	1.147	1.022	0.913	0.830	0.1182	5.294	4.554	3.927	3.449	3.076
0.0266	1.554	1.363	1.211	1.081	0.981	0.1679	8.948	7.632	6.528	5.690	5.031
0.0372	1.832	1.601	1.414	1.254	1.137						
PVP + Methanol											
0.0000	0.588	0.549	0.516	0.474	0.447	0.0253	0.839	0.777	0.724	0.669	0.627
0.0020	0.605	0.565	0.531	0.488	0.458	0.0303	0.896	0.829	0.772	0.711	0.668
0.0029	0.613	0.572	0.537	0.494	0.463	0.0414	1.037	0.958	0.890	0.821	0.771
0.0050	0.630	0.587	0.552	0.507	0.476	0.0532	1.204	1.108	1.029	0.948	0.882
0.0080	0.658	0.613	0.575	0.529	0.496	0.0659	1.396	1.285	1.186	1.096	1.022
0.0101	0.678	0.633	0.591	0.542	0.509	0.0806	1.599	1.472	1.353	1.252	1.161
0.0152	0.730	0.678	0.633	0.584	0.548	0.1088	2.150	1.978	1.806	1.658	1.550
0.0204	0.782	0.725	0.676	0.625	0.582						
PVP + Ethanol											
0.0000	1.205	1.093	0.994	0.907	0.834	0.0253	1.755	1.583	1.434	1.303	1.191
0.0020	1.243	1.128	1.026	0.931	0.860	0.0309	1.904	1.714	1.544	1.414	1.285
0.0030	1.260	1.144	1.040	0.946	0.871	0.0416	2.205	1.974	1.778	1.615	1.474
0.0050	1.292	1.170	1.062	0.970	0.891	0.0523	2.554	2.291	2.047	1.859	1.698
0.0080	1.348	1.221	1.109	1.012	0.933	0.0671	3.036	2.706	2.428	2.192	1.999
0.0101	1.384	1.255	1.142	1.040	0.958	0.0784	3.517	3.109	2.786	2.528	2.283
0.0149	1.495	1.351	1.226	1.116	1.024	0.0941	4.198	3.754	3.326	3.033	2.755
0.0203	1.624	1.468	1.332	1.208	1.104	0.1104	4.987	4.410	3.924	3.545	3.255
PVP + Acetonitrile											
0.0000	0.368	0.354	0.343	0.315	0.298	0.0414	0.519	0.494	0.473	0.441	0.419
0.0020	0.374	0.359	0.347	0.318	0.302	0.0516	0.564	0.539	0.513	0.479	0.457
0.0050	0.383	0.367	0.355	0.325	0.309	0.0664	0.644	0.609	0.580	0.543	0.519
0.0081	0.391	0.376	0.362	0.332	0.315	0.0805	0.730	0.690	0.654	0.612	0.584
0.0101	0.398	0.382	0.369	0.339	0.321	0.0953	0.846	0.787	0.746	0.703	0.665
0.0202	0.432	0.414	0.399	0.369	0.351	0.1103	0.975	0.913	0.856	0.803	0.763
0.0307	0.473	0.451	0.432	0.403	0.384						

Table 3. Continued

m_{wp}	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	m_{wp}	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
					PVP + 1-Propanol						
0.0000	2.197	1.947	1.726	1.542	1.379	0.0309	3.771	3.309	2.908	2.570	2.313
0.0020	2.278	2.017	1.788	1.595	1.439	0.0417	4.441	3.868	3.402	3.000	2.679
0.0030	2.319	2.053	1.818	1.622	1.463	0.0526	5.240	4.574	3.999	3.533	3.146
0.0050	2.404	2.131	1.885	1.682	1.518	0.0671	6.388	5.538	4.822	4.264	3.780
0.0080	2.549	2.253	2.001	1.779	1.602	0.0797	7.575	6.575	5.719	5.035	4.447
0.0101	2.642	2.333	2.079	1.839	1.651	0.0963	9.261	7.964	6.924	6.072	5.385
0.0152	2.903	2.550	2.256	2.002	1.796	0.1094	11.064	9.546	8.245	7.265	6.416
0.0203	3.167	2.785	2.456	2.180	1.959						
					PVP + 2-Propanol						
0.0000	2.404	2.072	1.777	1.543	1.357	0.0253	3.645	3.118	2.652	2.280	1.997
0.0020	2.458	2.110	1.814	1.570	1.373	0.0309	3.923	3.330	2.827	2.437	2.126
0.0030	2.512	2.154	1.852	1.606	1.404	0.0416	4.505	3.830	3.257	2.803	2.446
0.0050	2.612	2.235	1.925	1.666	1.456	0.0526	5.263	4.449	3.771	3.253	2.814
0.0081	2.737	2.335	2.004	1.741	1.527	0.0666	6.374	5.347	4.531	3.874	3.362
0.0101	2.853	2.434	2.089	1.812	1.583	0.0802	7.439	6.217	5.286	4.566	4.046
0.0152	3.095	2.625	2.253	1.944	1.705	0.0964	8.999	7.514	6.382	5.441	4.723
0.0200	3.358	2.853	2.440	2.102	1.842	0.1100	10.413	8.663	7.328	6.281	5.438
					PVP + 1-Butanol						
0.0000	2.937	2.569	2.260	1.998	1.784	0.0416	5.899	5.053	4.412	3.876	3.424
0.0020	3.012	2.641	2.310	2.044	1.824	0.0525	6.819	5.879	5.091	4.468	3.936
0.0050	3.194	2.797	2.453	2.163	1.923	0.0670	8.218	7.022	6.046	5.270	4.647
0.0081	3.388	2.960	2.598	2.286	2.036	0.0806	10.061	8.525	7.342	6.350	5.592
0.0099	3.501	3.048	2.675	2.362	2.107	0.0964	12.060	10.255	8.890	7.621	6.684
0.0204	4.185	3.628	3.194	2.844	2.479	0.1088	13.989	11.760	10.087	8.727	7.632
0.0309	4.949	4.289	3.791	3.355	2.919						

dominant contribution to the total value of κ_s, and therefore the effect of temperature on the isentropic compressibility of the investigated PVP solutions is similar to the temperature dependency of isentropic compressibility of pure solvents. The isentropic compressibilities for both pure nonaqueous solvents and polymer increase with increasing temperature. Therefore, it can be expected that the isentropic compressibilities of the nonaqueous PVP solutions increase by increasing temperature. However, in the case of the PVP + water system, for the temperature range investigated in this work (288.15 to 313.15) K, $d\kappa_s$(solute intrinsic)/$dT > 0$ and $d\kappa_s$(solvent intrinsic)/$dT < 0$. It can be expected that at polymer concentrations higher than 0.41 the isentropic compressibility isotherms of aqueous solution of PVP intersect. In fact, the κ_s(solvent intrinsic) is the dominant contribution to the total value of κ_s from pure water up to the converging concentration, and beyond that κ_s(solute intrinsic) is the substantial contribution.

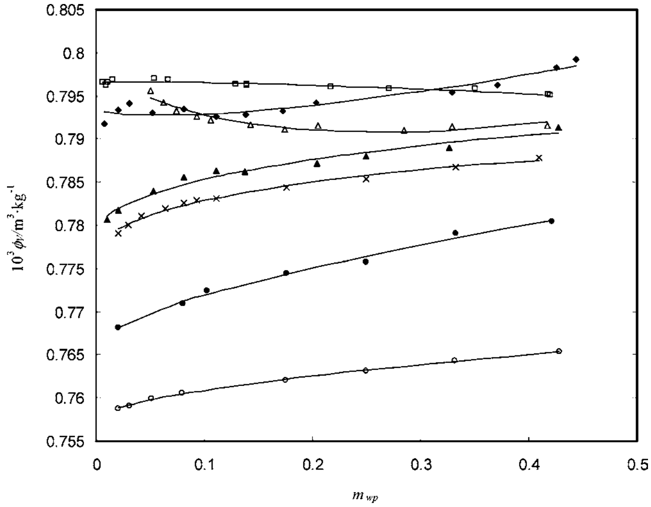

Figure 1. Variation of the apparent specific volume of PVP, ϕ_V, as a function of polymer weight molality, m_{wp}, in different solvents investigated in this work at T = 298.15 K: ○, methanol; ●, ethanol; ×, 2-propanol; ▲, 1-propanol; △, acetonitrile; ◆, butanol; □, water; —, calculated by eq 5.

As can be seen from Figure 7, the solute concentration dependence of κ_s for aqueous and nonaqueous solutions of PVP, respectively, becomes greater and smaller as temperature decreases. At each temperature, the magnitudes of $\kappa_s - \kappa_{s0}$ for the investigated solutions follow the order: methanol > ethanol ≈ 2-propanol > 1-propanol > 1-butanol > acetonitrile > water. It has been shown that[45] for aqueous solutions of electrolytes with large hydration numbers, such as $MgSO_4$ and Na_2SO_4, the concentration dependence of κ_s is more negative than electrolytes such as NaCl with small hydration numbers. If we accept the similar behavior for aqueous and nonaqueous polymer solutions, we can conclude that the PVP−solvent interactions follow the order: methanol > ethanol ≈ 2-propanol > 1-propanol > 1-butanol > acetonitrile > water.

As can be seen from Table 5, the infinite dilution apparent specific isentropic compressibilities of PVP in water and acetonitrile have positive values, and in the other investigated solvents have negative values. The negative values of ϕ_K indicate that the solvent molecules surrounding the solute molecules would present greater resistance to compression than the bulk. This behavior occurs in the case of strong solvent−solute interactions. On the other hand, the positive values of ϕ_K indicate that the solvent molecules around the solute molecules are more compressible than the solvent molecules in the bulk solution. This behavior occurs in the case of weak solvent−solute interactions. The results show that the values of ϕ_K^0 for PVP in nonaqueous solutions decrease as temperature increases; however, these values in aqueous solutions increase by increasing temperature. Table 5 also shows that, at each temperature, the values of ϕ_K^0 for PVP in the investigated solvents follow the order: acetonitrile > water > 1-butanol > 1-propanol > ethanol ≈ 2-propanol > methanol. From the temperature dependence of ϕ_K^0 and $\kappa_s - \kappa_{s0}$, we can conclude that the PVP−water and PVP−nonaqueous solvents interactions respectively become weaker and stronger as temperature increases. The temperature

Table 4. Infinite Dilution Partial Specific Volume, ϕ_V^0/(m^3·kg^{-1}), and Empirical Constant, b_V/(m^3·kg^{-1}) and b_{VV}/(m^3·kg^{-1}), of Equation 4 for Different Systems Investigated in This Work at Different Temperatures, *T*

T/K = 288.15			*T*/K = 293.15			*T*/K = 298.15			*T*/K = 303.15			*T*/K = 308.15			*T*/K = 313.15		
$10^3\ \phi_V^0$	$10^3\ b_V$	$10^3\ b_{VV}$	$10^3\ \phi_V^0$	$10^3\ b_V$	$10^3\ b_{VV}$	$10^3\ \phi_V^0$	$10^3\ b_V$	$10^3\ b_{VV}$	$10^3\ \phi_V^0$	$10^3\ b_V$	$10^3\ b_{VV}$	$10^3\ \phi_V^0$	$10^3\ b_V$	$10^3\ b_{VV}$	$10^3\ \phi_V^0$	$10^3\ b_V$	$10^3\ b_{VV}$
PVP + Water																	
0.79025	0.00268	−0.01022	0.79338	0.00184	−0.00877	0.79655	0.00062	−0.00681	0.79927	0.00096	−0.00701	0.80208	0.00080	−0.00632	0.80487	0.00070	−0.00574
PVP + Methanol																	
0.75612	0.01079	0.00227	0.75673	0.01104	0.00228	0.75717	0.01152	0.00229	0.75742	0.01226	0.00231	0.75757	0.01311	0.00233	0.75813	0.01267	0.00371
PVP + Ethanol																	
0.76366	0.01819	0.00981	0.76457	0.01879	0.00953	0.76521	0.02043	0.00762	0.76647	0.01986	0.00887	0.76745	0.02017	0.00907	0.76857	0.02007	0.00949
PVP + Acetonitrile																	
0.79917	−0.02983	0.03699	0.80011	−0.03002	0.03783	0.8012	−0.03054	0.03892	0.80221	−0.03106	0.04012	0.80300	−0.03110	0.04078	0.80380	−0.03131	0.04158
PVP + 1-Propanol																	
0.77642	0.01789	−0.00075	0.77806	0.01812	−0.00213	0.77901	0.02056	−0.00630	0.78159	0.01779	−0.00337	0.78345	0.01711	−0.00290	0.78536	0.01629	−0.00228
PVP + 2-Propanol																	
0.77302	0.02161	−0.00664	0.77517	0.01996	−0.00606	0.77664	0.02048	−0.00847	0.77873	0.01840	−0.00665	0.78019	0.01809	−0.00717	0.78182	0.01669	−0.00576
PVP + 1-Butanol																	
0.78876	−0.00082	0.02317	0.79088	−0.00213	0.02488	0.79357	−0.00492	0.02787	0.79595	−0.00669	0.02927	0.79873	−0.00989	0.03285	0.80082	−0.01077	0.03341

Table 5. Infinite Dilution Partial Specific Isentropic Compressibility, ϕ_K^0/ (m^3·kg^{-1}·Pa^{-1}), and Empirical Constant, b_K/(m^3·kg^{-1}·Pa^{-1}) and b_{KK}/(m^3·kg^{-1}·Pa^{-1}), of Equation 5 for Different Systems Investigated in This Work at Different Temperatures, *T*

T/K = 288.15			*T*/K = 293.15			*T*/K = 298.15			*T*/K = 303.15			*T*/K = 308.15			*T*/K = 313.15		
$10^{13}\ \phi_K^0$	$10^{13}\ b_K$	$10^{13}\ b_{KK}$	$10^{13}\ \phi_K^0$	$10^{13}\ b_K$	$10^{13}\ b_{KK}$	$10^{13}\ \phi_K^0$	$10^{13}\ b_K$	$10^{13}\ b_{KK}$	$10^{13}\ \phi_K^0$	$10^{13}\ b_K$	$10^{13}\ b_{KK}$	$10^{13}\ \phi_K^0$	$10^{13}\ b_K$	$10^{13}\ b_{KK}$	$10^{13}\ \phi_K^0$	$10^{13}\ b_K$	$10^{13}\ b_{KK}$
PVP + Water																	
−0.38476	0.86543	−0.61986	0.13422	−0.15461	0.66987	0.40401	−0.43716	0.98399	0.61466	−0.59591	1.14965	0.76461	−0.61078	1.13804	0.87310	−0.52515	0.99230
PVP + Methanol																	
−3.34060	1.87548	−0.33991	−3.57754	1.76808	−0.03713	−3.9194	1.93181	−0.0777	−4.23943	1.91446	0.18685	−4.61428	2.02766	0.25513	−4.96078	1.97599	0.54162
PVP + Ethanol																	
−2.84956	1.77349	0.81752	−3.15878	1.94252	0.90344	−3.53796	2.34266	0.61202	−3.79385	2.24562	1.03529	−4.1597	2.47658	1.01482	−4.49661	2.57785	1.12761
PVP + Acetonitrile																	
1.40869	−0.03642	−0.52646	1.40974	−0.15951	−0.37433	1.38122	−0.21733	−0.31037	1.36825	−0.34548	−0.16075	1.32601	−0.41415	−0.09874	1.28389	−0.51525	0.01437
PVP + 1-Propanol																	
−1.45032	1.3389	0.31126	−1.69052	1.69171	−0.07718	−2.07842	2.48052	−1.0661	−2.14333	2.16340	−0.40147	−2.31421	2.19398	−0.39834	−2.48527	2.18823	−0.28812
PVP + 2-Propanol																	
−3.08398	2.65175	−0.49963	−3.30294	2.65954	−0.33842	−3.48098	2.50107	0.01469	−3.75051	2.54316	0.13748	−4.07942	2.73749	−0.00100	−4.36934	2.67690	0.27445
PVP + 1-Butanol																	
−0.68778	1.36226	−0.43988	−0.89798	1.75255	−0.87477	−0.96155	1.65154	−0.6718	−1.09617	1.75344	−0.73151	−1.1921	1.73155	−0.66192	−1.35181	1.88804	−0.82203

Table 6. Deviations of Equations 4 and 5 for the Correlation of the Infinite Dilution Partial Specific Volume, $\phi_V^0/(\mathrm{m^3 \cdot kg^{-1}})$, and Partial Specific Isentropic Compressibility, $\phi_K^0/(\mathrm{m^3 \cdot kg^{-1} \cdot Pa^{-1}})$, of the Investigated PVP Solutions

system	deviations in ϕ_V^0						deviations in ϕ_K^0					
	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
PVP + water	0.029[a]	0.024	0.022	0.021	0.022	0.021	−0.533[a]	10.196	5.394	3.948	3.002	2.399
PVP + methanol	0.009	0.013	0.012	0.015	0.016	0.012	−3.022	−2.734	−2.766	−2.550	−2.418	−2.319
PVP + ethanol	0.037	0.039	0.039	0.040	0.042	0.041	−1.030	−0.889	−0.917	−0.848	−0.873	−0.799
PVP + acetonitrile	0.044	0.045	0.045	0.046	0.047	0.047	0.544	0.464	0.440	0.464	0.561	0.731
PVP + 1-propanol	0.050	0.053	0.060	0.054	0.053	0.053	−2.472	−2.724	−3.766	−3.260	−2.792	−2.509
PVP + 2-propanol	0.027	0.027	0.031	0.027	0.030	0.030	−0.783	−0.774	−0.721	−0.659	−0.593	−0.519
PVP + 1-butanol	0.062	0.073	0.071	0.071	0.068	0.074	−34.702	1.220	−9.779	−5.619	−4.295	−4.280

[a] Dev $= 100/\mathrm{NP}\sum[|\phi_{\mathrm{exp}}^0 - \phi_{\mathrm{cal}}^0|/\phi_{\mathrm{exp}}^0]$.

Table 7. Comparison of the Infinite Dilution Partial Specific Volume, $10^3\ \phi_V^0/(\mathrm{m^3 \cdot kg^{-1}})$, for PVP in Water, Methanol, Ethanol, and 1-Propanol Obtained in This Study with Literature (Refs 3 and 7) Values at T = (298.15 and 308.15) K

	this work		literature values	
system	T/K = 298.15	T/K = 308.15	T/K = 298.15	T/K = 308.15
PVP + water	0.79655	0.80208	0.7986[3]	0.8044[3]
PVP + methanol	0.75717	0.75757	0.7798[7]	0.8062[7]
PVP + ethanol	0.76521	0.76745	0.8391[7]	0.9423[7]
PVP + 1-propanol	0.77901	0.78345	0.7939[7]	0.8140[7]

dependence of solvent activity in aqueous[3] and nonaqueous[46] polymer solutions also supports this behavior. It has been found that the water activities of aqueous PVP solutions increase with increasing temperature.[3] However, solvent activities in nonaqueous polymer solutions decrease as temperature increases.[46]

As can be seen from Figure 8, for polymer weight molalities smaller than 0.035, the magnitudes of the measured viscosity data have the order of acetonitrile < methanol < water < ethanol < 1-propanol < 2-propanol < 1-butanol. For polymer weight molalities higher than 0.035, the position of 1-propanol and

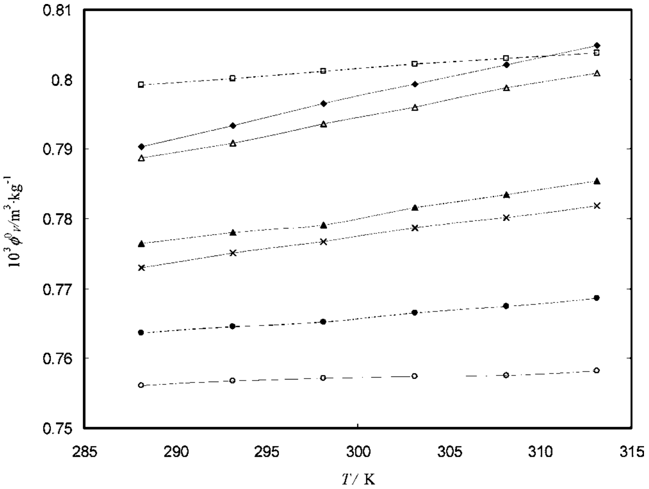

Figure 2. Variation of the infinite dilution apparent specific volume of PVP, ϕ_V^0, in different solvents investigated in this work as a function of temperature, T: ○, methanol; ●, ethanol; ×, 2-propanol; ▲, 1-propanol; △, butanol; ◆, water; □, acetonitrile.

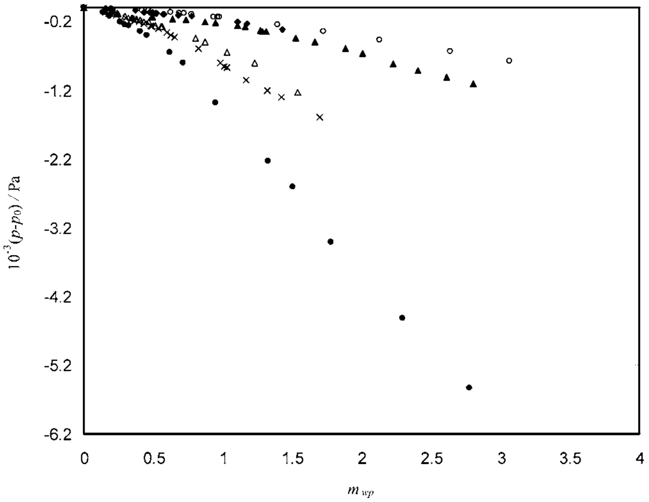

Figure 3. Vapor pressure depression, $p - p_0$, of solutions of PVP in various solvents as a function of polymer weight molality, m_{wp}, at T = 298.15 K: ◆, butanol;[4] △, 2-propanol;[4] ×, ethanol;[4] ●, methanol;[4] ○, water;[3] ▲, acetonitrile.[5]

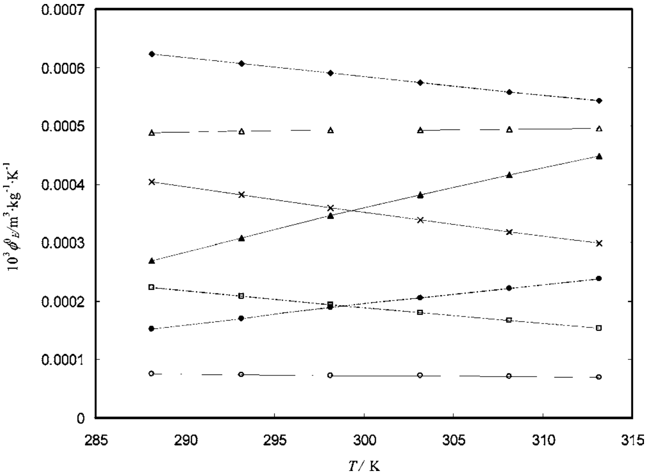

Figure 4. Variation of the infinite dilution apparent specific expansibility of PVP, ϕ_E^0, in different solvents investigated in this work as a function of temperature, T: ○, methanol; ●, ethanol; ×, 2-propanol; ▲, 1-propanol; △, butanol; ◆, water; □, acetonitrile.

Table 8. Fitting Parameters, *a*, *b*, and *c*, of Equation 7

parameter system	a	b	c	dev[a]
PVP + water	−1.04604	−0.02632	0.40313	0.006
PVP + methanol	0.65434	0.00068	0.01596	0.014
PVP + ethanol	3.17731	0.08560	−0.68274	0.009
PVP + acetonitrile	−0.96951	−0.04514	0.44758	0.005
PVP + 1-propanol	5.77393	0.17485	−1.40648	0.026
PVP + 2-propanol	−1.88087	−0.06413	0.66082	0.013
PVP + 1-butanol	1.22658	0.03975	−0.19647	0.017

[a] Dev $= 100/\mathrm{NP}\sum[|\phi^0_{\mathrm{exp}} - \phi^0_{\mathrm{cal}}|/\phi^0_{\mathrm{exp}}]$.

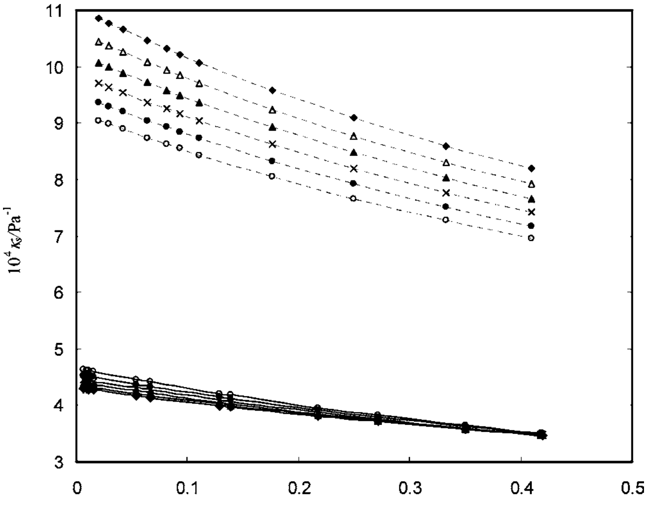

Figure 5. Variation of the isentropic compressibility, κ_s, of solutions of PVP in water (solid lines) and in 2-propanol (dotted lines) as a function of polymer weight molality, m_{wp}, at different temperatures: ○, $T = 288.15$ K; ●, $T = 293.15$ K; ×, $T = 298.15$ K; ▲, $T = 303.15$ K; △, $T = 308.15$ K; ◆, $T = 313.15$ K.

2-propanol in this order is exchanged. Figure 9 shows that the polymer concentration dependence of viscosity for the investigated solutions of PVP becomes greater as temperature decreases. Furthermore, at each temperature and polymer concentration, the magnitudes of $\eta - \eta_0$ for the investigated solutions follow the order: acetonitrile < methanol < water < ethanol < 2-propanol < 1-propanol < 1-butanol.

In this work, the segment-based local composition Wilson[47] and nonrandom two-liquid (NRTL)[48] models developed for the viscosity of polymer solutions were used for the correlation of

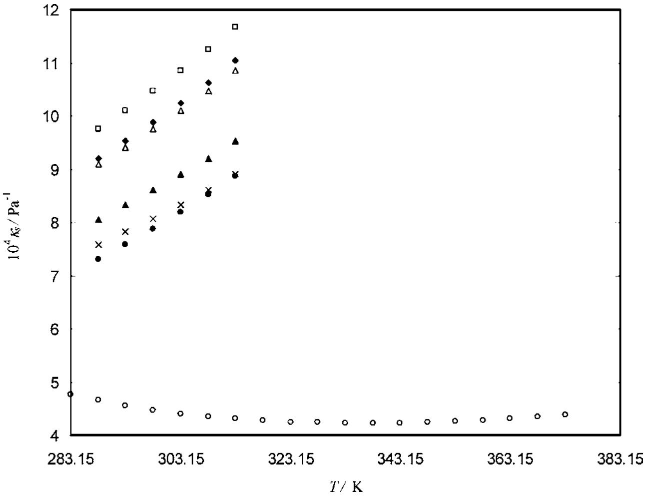

Figure 6. Variation of the isentropic compressibility, κ_s, as a function of temperature, T, for pure components: ○, water; ●, acetonitrile; ×, 1-butanol; ▲, 1-propanol; △, ethanol; ◆, 2-propanol; □, methanol.

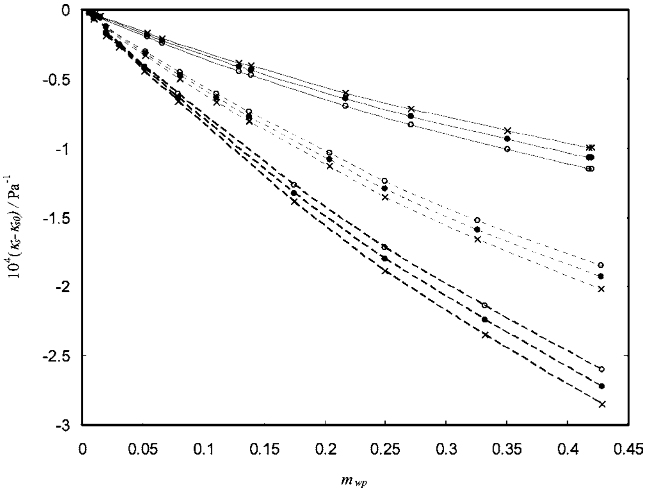

Figure 7. Variation of $\kappa_s - \kappa_{s0}$ of solutions of PVP in water (solid lines), in 1-propanol (dotted lines) and in methanol (dashed lines) as a function of polymer weight molality, m_{wp}, at different temperatures: ○, $T = 288.15$ K; ●, $T = 293.15$ K; ×, $T = 298.15$ K.

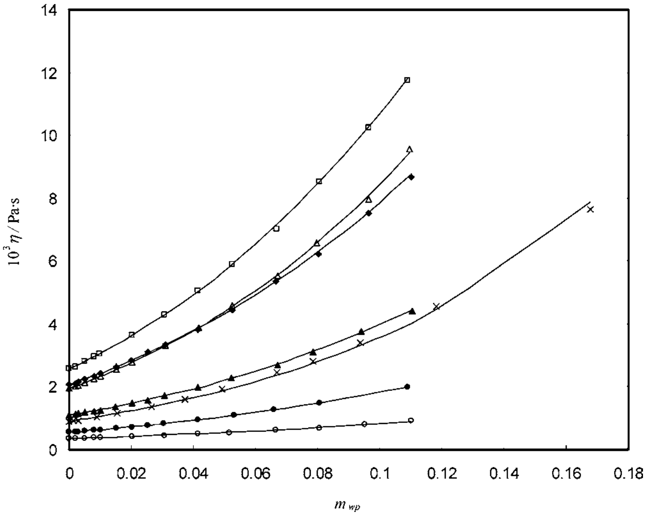

Figure 8. Variation of the viscosities, η, of solutions of PVP in different solvents as a function of polymer weight molality, m_{wp}, at $T = 298.15$ K: ○, acetonitrile; ●, methanol; ×, water; ▲, ethanol; △, 1-propanol; ◆, 2-propanol; □, 1-butanol; —, calculated by Wilson model.

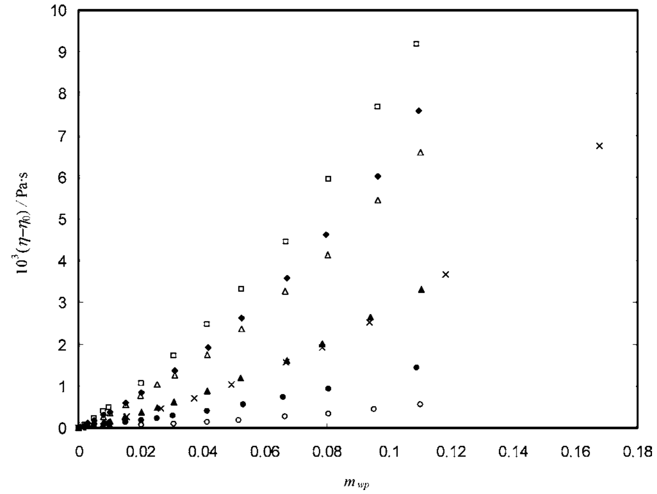

Figure 9. Variation of, $\eta - \eta_0$, of solutions of PVP in different solvents as a function of polymer weight molality, m_{wp}, at $T = 298.15$ K: ○, acetonitrile; ●, methanol; ×, water; ▲, ethanol; △, 2-propanol; ◆, 1-propanol; □, 1-butanol.

the obtained viscosity data. These models use a combination of the segment-based Eyring mixture viscosity model for the ideal contribution and the segment-based Wilson and NRTL models for correction or excess term. These models for a multicomponent polymer solution have the following forms:

$$\ln(\eta V) = \sum_{i} X_i \ln(\eta_i \bar{V}_i) + \frac{g^{E*}_{(\text{Wilson or NRTL})}}{RT} \tag{8}$$

$$V = \sum_{i} X_i \bar{V}_i \tag{9}$$

$$\eta_i = \sum_{I} r_{i,I} \eta_I / (\sum_{I} r_{i,I}) \tag{10}$$

$$\bar{V}_i = \sum_{I} r_{i,I} V_{i,I} / (\sum_{I} r_{i,I}) \tag{11}$$

$$X_i = \sum_{I} r_{i,I} x_I / (\sum_{J} \sum_{j} r_{j,J} x_J) \tag{12}$$

$$\frac{g^{E*}_{\text{Wilson}}}{RT} = -C \sum_{i} X_i \ln\left(\sum_{j} X_j \exp\left(-\frac{E_{ji}}{CRT}\right)\right) \tag{13}$$

$$\frac{g^{E*}_{\text{NRTL}}}{RT} = \sum_{i} X_i \left(\frac{\sum_{j} X_j \frac{a_{ji}}{RT} \exp\left(-\alpha \frac{a_{ji}}{RT}\right)}{\sum_{k} X_k \exp\left(-\alpha \frac{a_{ki}}{RT}\right)} \right) \tag{14}$$

where $r_{i,I}$ is the number of the segments i in component I, $V_{i,I}$ is the molar volume of the segment i in component I, X_i is the segment-based mole fraction of component i, α is the nonrandomness factor, which was fixed at 0.25, and C is the effective coordination number which was fixed at 10. In the above relations the species i, j, and k can be solvent molecules or segments, and species I and J can be solvent or polymer molecules. The applicability of these viscosity models has been

Table 9. Parameters of the Segment-Based Eyring−NRTL and Wilson Models Along with the Corresponding Deviations for the Investigated PVP Solutions

	NRTL					Wilson				
parameter system	a	b	a_{ps}	a_{sp}	dev %	a	b	E_{ps}	E_{sp}	dev %[a]
			J·mol^{-1}	J·mol^{-1}				J·mol^{-1}	J·mol^{-1}	
PVP (p) + water (s)	$1.7111 \cdot 10^{-7}$	$2.8994 \cdot 10^{+4}$	−12.0255	$4.6352 \cdot 10^{+4}$	3.13	$1.2177 \cdot 10^{-8}$	$1.9434 \cdot 10^{+4}$	$2.4438 \cdot 10^{+3}$	$1.939 \cdot 10^{+5}$	1.65
PVP (p) + methanol (s)	$3.3428 \cdot 10^{-3}$	$1.2157 \cdot 10^{+4}$	$5.0072 \cdot 10^{+3}$	$3.9584 \cdot 10^{+4}$	0.75	$6.616 \cdot 10^{-6}$	$4.1646 \cdot 10^{+3}$	$1.0767 \cdot 10^{+5}$	$9.7106 \cdot 10^{+4}$	0.58
PVP (p) + ethanol (s)	0.0153	$8.6499 \cdot 10^{+3}$	$4.8102 \cdot 10^{+3}$	$2.7158 \cdot 10^{+4}$	0.58	$1.3964 \cdot 10^{-5}$	$3.7702 \cdot 10^{+3}$	$3.7994 \cdot 10^{+5}$	$6.2205 \cdot 10^{+4}$	0.53
PVP (p) + acetonotrile (s)	$1.5513 \cdot 10^{+5}$	$4.3135 \cdot 10^{+3}$	$4.476 \cdot 10^{+4}$	$-1.0234 \cdot 10^{+4}$	1.26	15.9728	$5.7284 \cdot 10^{+4}$	$4.4989 \cdot 10^{+5}$	$-4.5244 \cdot 10^{+5}$	1.21
PVP (p) + 1-propanol (s)	$2.2515 \cdot 10^{-5}$	$9.9769 \cdot 10^{+3}$	$3.8052 \cdot 10^{+3}$	$3.1128 \cdot 10^{+4}$	0.44	$9.2078 \cdot 10^{-6}$	$8.2285 \cdot 10^{+3}$	$-1.7794 \cdot 10^{+4}$	$7.3549 \cdot 10^{+4}$	0.44
PVP (p) + 2-propanol (s)	$1.1617 \cdot 10^{-5}$	$9.2669 \cdot 10^{+3}$	$4.5572 \cdot 10^{+3}$	$2.7709 \cdot 10^{+4}$	0.64	$2.1104 \cdot 10^{-4}$	$4.3812 \cdot 10^{+3}$	−60.007	$6.2266 \cdot 10^{+4}$	0.62
PVP (p) + 1-butanol (s)	$7.8182 \cdot 10^{-7}$	$9.4033 \cdot 10^{+3}$	$2.9887 \cdot 10^{+3}$	$2.6107 \cdot 10^{+4}$	0.67	$1.1585 \cdot 10^{-5}$	$5.0287 \cdot 10^{+3}$	−16.3371	$5.5906 \cdot 10^{+4}$	0.60

[a] Dev % $= 100/\text{NP}\sum_{I=1}^{\text{NP}} |\eta_I^{\text{exp}} - \eta_I^{\text{cal}}|/\eta_I^{\text{exp}}$. NP is the number of experimental data points.

tested using the experimental viscosity data obtained in this work. A value of $r = 1$ was used for solvents, and for the polymer the value of r is ratio of the molar mass of the polymer to that of the segment. The value of the molar volume of segment was calculated from the ratio of the molar volume of the polymer to its degree of polymerization. The molar volume of the polymer was calculated from the infinite dilution apparent specific volume of polymer given in Table 4. The following relation was used to consider the temperature dependence of the pure polymer viscosity:

$$\eta_{\mathrm{p}} = a\exp(b/T) \tag{15}$$

The evaluated parameters along with the corresponding deviations for the systems studied are listed in Table 9. The model parameters are independent of temperature. On the basis of the obtained deviations given in Table 9, we conclude that, although both models represent the experimental viscosity data of the investigated polymer solutions with good accuracy, the obtained deviations for the Wilson model are smaller than those for the NRTL model. Comparison between the experimental and the correlated viscosity data by the Wilson model are shown in Figure 8.

Conclusions

The values of ϕ_V^0 for PVP in the investigated solvents increased along with an increase in temperature and at each temperature follow the order: methanol < ethanol < 2-propanol < 1-propanol < butanol < water < acetonitrile. The values of ϕ_{E}^0 for PVP in water, methanol, 2-propanol, and acetonitrile decrease by increasing temperature; however, those in ethanol, 1-propanol, and 1-butanol increase by increasing temperature. The infinite dilution apparent specific isentropic compressibilities, ϕ_K^0, of PVP in water and acetonitrile have positive values and in the other investigated solvents have negative values. The results show that the values of ϕ_K^0 for PVP in nonaqueous solutions decrease as temperature increases; however, these values in aqueous solutions increase by increasing temperature. At each temperature, the values of ϕ_K^0 of PVP in the investigated solvents follow the order: acetonitrile > water > 1-butanol > 1-propanol > ethanol ≈ 2-propanol > methanol. In the second part of this work, the viscosity measurements at $T = (293.15, 298.15, 303.15, 308.15, \text{and } 313.15)$ K were carried out for the investigated binary PVP solutions, and the results were correlated successfully with the segment-based Eyring-Wilson and NRTL viscosity models. It was found that the Wilson model produces better results than the NRTL model. The polymer concentration dependence of viscosity of the investigated PVP solutions becomes greater as temperature decreases, and at the same conditions, the magnitudes of both of η and $\eta - \eta_0$ follow the order: acetonitrile < methanol < water < ethanol < 2-propanol < 1-propanol < 1-butanol.

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