Vapor−Liquid Equilibria, Density, and Speed of Sound for the System Poly(ethylene glycol) 400 + Methanol at Different Temperatures

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Solvent activity measurements have been performed on the system poly(ethylene glycol) 400 (PEG 400) + methanol at T = (298.15 to 328.15) K using the improved isopiestic method. The obtained solvent activity data were correlated with the original and modified Flory−Huggins models. It was found that for the studied system at any mass fraction, as the temperature is increased the solvent activity and Flory parameter are both decreased, indicating an increase of interaction between polymer and methanol as the temperature is increased. The density and speed of sound data were also measured at T = (288.15 to 328.15) K for the PEG 400 + methanol system. From the obtained density values, the excess molar volume data were calculated and fitted to the Redlich−Kister equation. The excess molar isentropic compression values calculated from the measured speed of sound and density data were also fitted to the Redlich−Kister equation.

Introduction

In recent years, numerous studies have been carried out on mixtures containing poly(ethylene glycols) (PEGs). PEG has numerous uses in biotechnology,[1,2] in chemical partitioning,[3−5] and in extractive crystallization of inorganic salts.[6] An understanding of the thermodynamics of the polymer solutions is important in practical applications such as polymerizations, devolatilization, and the incorporation of plasticizers and other additives. Diffusion phenomenon in polymer melts and solutions are strongly affected by nonideal solution behavior, since the chemical potential rather than the concentration provides the driving force for diffusion. Proper design and engineering of many polymer processes depend greatly upon accurate modeling of thermodynamic parameters such as solvent activities.

The vapor−liquid data have been compiled by Wohlfarth[7] for some polymer + solvent systems. Recently, in regard with PEG + alcohol solutions, a few vapor pressure data for the PEG + methanol and PEG + ethanol systems with polymer of molar mass 600 have been measured[8] at 303.15 K by an apparatus based on the principle of electromicrobalance. In their vapor sorption measurements,[8] however, they only considered the methanol and ethanol mass fractions in the limited ranges of 0.0143 to 0.3385 and 0.0298 to 0.3827, respectively. There are also vapor pressure or activity data for PEG + 2-propanol[9] with different molar mass of PEG. However, as far as we know there is no vapor pressure or activity data for the PEG400 + methanol system at different temperatures in the literature. In this work, solvent activity data for PEG 400 + methanol were measured at T = (298.15 to 328.15) K using the improved isopiestic method. The recent vapor pressure measurements on the solutions of LiBr in methanol[10] provide us the osmotic coefficients of these solutions in wide ranges of concentrations and at different temperatures. These osmotic coefficient data permit us to use LiBr in methanol systems as an isopiestic standard; therefore, isopiestic measurement is now possible at higher concentrations and temperatures for solutions of other salts or polymer in methanol than was possible before.

For PEG 400 + methanol, density and speed of sound data were also measured at T = (288.15 to 328.15) K, from which the values for excess molar volume and isentropic compression were calculated. For this system, there is no density or speed of sound data at different temperatures in the literature. The variation of activity, excess molar volume, and excess molar isentropic compression values with the polymer concentration and temperature provide us useful information in regard to polymer−solvent interactions and deviation of polymer solution from ideal solution.

Experimental Procedures

Materials. All the chemicals were obtained from Merck. Lithium bromide with purity of minimum mass fraction 0.995 was dried in an electrical oven at about 110 °C for 24 h prior to use. Methanol with purity of minimum mass fraction 0.995 was dehydrated according to Vogel.[11] Double-distilled, deionized water was used. For molar mass of PEG, the value 400 $g \cdot mol^{-1}$ was used.

Apparatus and Procedures. The isopiestic apparatus employed is essentially similar to the one used previously.[12] Recently this technique has been used for the measurement of activity of the methanol in alcohol + poly(vinyl pyrrolidone),[13] alcohol + poly(propylene glycol),[14] and 2-propanol in 2-propanol + poly(ethylene glycol)[9] systems with different molar masses of the polymer. This apparatus consisted of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard LiBr solutions, two flasks contained PEG solutions, and the central flask was used as a methanol reservoir. The apparatus was held in a constant-temperature bath at least 120 h for equilibration at T = (298.15 to 328.18) K. The temperature was controlled to within ± 0.005 °C by a Heto temperature controller (Hetotherm PF, Heto Lab Equipment, Denmark). After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance (Shimatzu, 321-34553, Shimatzu Co., Japan) with an uncertainty of $\pm 1 \times 10^{-7}$ kg. It was assumed that the equilibrium condition was reached when the differences between the mass fractions of each duplicate were less than 1 %. In all

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Table 1. Experimental Isopiestic Mass Fraction *w*, Osmotic Coefficients Φ, and Methanol Activity a_1 for Methanol (1) + PEG400 (2) at Different Temperatures

w_{LiBr}	w_2	Φ_{LiBr}	a_1	p/kPa	w_{LiBr}	w_2	Φ_{LiBr}	a_1	p/kPa	w_{LiBr}	w_2	Φ_{LiBr}	a_1	p/kPa
T = 298.15 K														
0.0148	0.1076	0.909	0.9900	16.784	0.0963	0.4389	1.017	0.9232	15.637	0.2168	0.7307	1.665	0.7116	12.019
0.0190	0.1240	0.905	0.9871	16.734	0.1159	0.4993	1.087	0.9001	15.241	0.2395	0.7732	1.844	0.6514	10.993
0.0311	0.1547	0.900	0.9789	16.593	0.1260	0.5276	1.128	0.8869	15.015	0.2569	0.8033	1.995	0.6012	10.139
0.0411	0.2298	0.904	0.9718	16.472	0.1786	0.6538	1.403	0.7985	13.502	0.2875	0.8570	2.294	0.5050	8.506
0.0580	0.3028	0.924	0.9588	16.248	0.1836	0.6688	1.435	0.7881	13.325	0.2966	0.8643	2.391	0.4752	8.001
0.0777	0.3770	0.964	0.9418	15.957	0.1936	0.6867	1.499	0.7669	12.962					
T = 308.15 K														
0.0146	0.0846	0.892	0.9903	27.684	0.1131	0.4867	1.075	0.9038	25.228	0.2167	0.7226	1.646	0.7146	19.881
0.0307	0.1664	0.876	0.9798	27.386	0.1335	0.5402	1.162	0.8763	24.449	0.2439	0.7788	1.854	0.6433	17.876
0.0431	0.2354	0.883	0.9711	27.138	0.1477	0.5830	1.230	0.8545	23.831	0.2643	0.8102	2.029	0.5839	16.208
0.0587	0.3008	0.908	0.9591	26.797	0.1638	0.6173	1.314	0.8271	23.056	0.2898	0.8515	2.273	0.5045	13.985
0.0772	0.3646	0.953	0.9429	26.337	0.1702	0.6353	1.349	0.8154	22.725	0.3218	0.8926	2.626	0.3987	11.032
0.0976	0.4381	1.017	0.9221	25.747	0.1886	0.6773	1.459	0.7785	21.683	0.3492	0.9214	2.976	0.3078	8.504
T = 318.15 K														
0.0370	0.1948	0.918	0.9743	43.380	0.1348	0.5358	1.156	0.8756	38.901	0.2654	0.8039	2.013	0.5848	25.817
0.0462	0.2430	0.920	0.9676	43.076	0.1488	0.5739	1.220	0.8543	37.937	0.2893	0.8392	2.234	0.5111	22.528
0.0616	0.3137	0.936	0.9557	42.535	0.1653	0.6098	1.305	0.8264	36.676	0.3154	0.8762	2.502	0.4273	18.800
0.0770	0.3682	0.964	0.9424	41.931	0.2042	0.6934	1.540	0.7471	33.099	0.3254	0.8876	2.614	0.3944	17.340
0.1054	0.4623	1.042	0.9134	40.614	0.2105	0.7094	1.583	0.7323	32.433					
0.1172	0.4888	1.084	0.8992	39.970	0.2517	0.7793	1.895	0.6248	27.607					
T = 328.15 K														
0.0198	0.1117	0.714	0.9848	22.686	0.0664	0.3313	0.806	0.9409	21.659	0.1607	0.6431	1.314	0.7658	17.577
0.0285	0.1688	0.724	0.9777	22.520	0.0983	0.4436	0.920	0.8991	20.682	0.1675	0.6618	1.375	0.7455	17.105
0.0304	0.1776	0.727	0.9761	22.482	0.1157	0.5042	1.005	0.8698	19.998	0.1825	0.7086	1.522	0.6973	15.987
0.0557	0.2859	0.777	0.9525	21.930	0.1446	0.5975	1.187	0.8082	18.563					

cases, averages of the duplicate are reported as the total isopiestic mass fraction. The uncertainty in the measurement of solvent activity was estimated to be ± 0.0002.

In this study, the ultrasonic velocity and density of PEG 400 + methanol mixtures were also measured at different temperatures with a digital vibrating-tube analyzer (Anton Paar DSA 5000, Austria) with a proportional temperature controller that kept the samples at working temperature with an uncertainty of 0.001 K. Recently this apparatus has been used for measurement of density and sound velocity of aqueous solutions of poly(propylene glycol).[15] The apparatus was calibrated at each temperature with distilled water and dry air. The apparatus was also tested with the density of a known molality of aqueous NaCl using the data of Pitzer et al.[16] The uncertainty of the instrument is ± 0.003 kg.m^{-3} for density and 0.1 m·s^{-1} for ultrasonic velocity.

Results and Discussion

Experimental Results. At isopiestic equilibrium, the activity of solvent in the reference and PEG solutions must be the same. Therefore, the isopiestic equilibrium mass fractions with reference standard solutions of LiBr in methanol as reported in Table 1, enabled the calculation of the solvent activity, a_1, in the solutions of methanol (1) + PEG (2) from that of reference solutions using the relation

$$\ln a_1 = -\upsilon m_{LiBr}\phi_{LiBr}M_s, \quad m_{LiBr} = \frac{w_{LiBr}}{M_{LiBr}(1 - w_{LiBr})} \qquad (1a,b)$$

where υ is the sum of stoichiometric numbers of anion and the cation in the reference solutions; m_{LiBr} and w_{LiBr} are respectively the substance concentration and mass fraction of LiBr, which is in isopiestic equilibrium with the polymer solutions; M_s and M_{LiBr} are respectively the molar masses of the solvent and LiBr; and ϕ_{LiBr} is the osmotic coefficient of the isopiestic reference standard, calculated at m_{LiBr}. The necessary ϕ_{LiBr} values at any m_{LiBr} were obtained from the fitted extended Pitzer ion interaction model of Archer equation:

$$\phi_{LiBr} = \left[1 - A_\phi\left(\frac{\sqrt{m_{LiBr}}}{1 + b\sqrt{m_{LiBr}}}\right)\right] + m_{LiBr}(\beta^{(0)} + \beta^{(1)} \exp[-\alpha_1\sqrt{m_{LiBr}}] + \beta^{(2)} \exp[-\alpha_2\sqrt{m_{LiBr}}]) + (m_{LiBr})^2(C^{(0)} + C^{(1)} \exp[-\alpha_3\sqrt{I}]) \qquad (2)$$

The parameters of eq 2 for LiBr in methanol solutions in the concentration range (0.0411 to 6.8675) mol·kg^{-1} and temperature range of T = (298.15 to 333.15) K have been reported by Nasirzadeh et al.[10] It was also shown that,[10] using $\alpha_1 = 2$, $\alpha_2 = 7$, $\alpha_3 = 1$, and $b = 3.2$, the osmotic coefficients ϕ_{LiBr} are reproducible with standard deviation of about 0.01 in the above concentration and temperature ranges. The obtained methanol activity data for the system methanol (1) + PEG400 (2) are given in Table 1. To see the effect of temperature on the methanol activity, the a_1 values were plotted versus polymer mass fractions at (298.15 and 328.15) K in Figure 1. As can be seen from Figure 1, for a given polymer mass fraction an increase in temperature causes a slight decrease in its activity value.

From the calculated solvent activity data, the vapor pressure of methanol solutions, p, were determined with the help of the following relation:

$$\ln(a_1) = \ln\left(\frac{p}{p^*}\right) + \frac{(B - V_s^*)(p - p^*)}{RT} \qquad (3)$$

where B, V_s^*, and p^* are the second virial coefficient, molar volume, and vapor pressure of pure methanol, respectively. The values of the physical properties for the methanol, which are taken from Nasirzadeh et al.,[10] are summarized in Table 2. The experimental vapor pressure data are also given in Table 1.

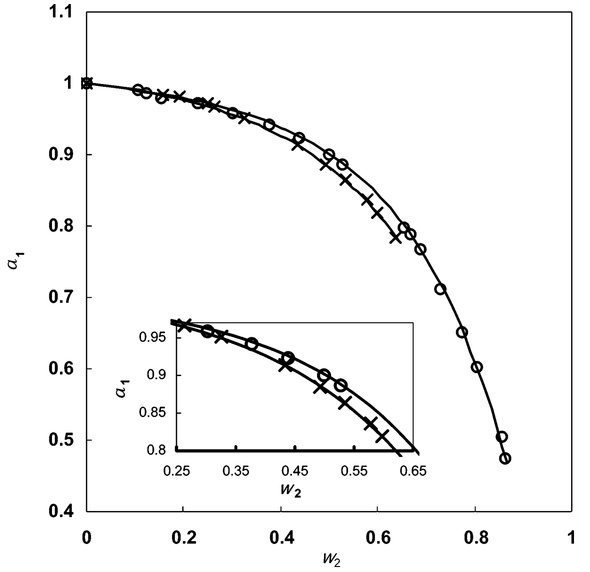

Figure 1. Experimental and calculated activity of methanol, a_1, plotted against mass fraction of polymer, w_2, for methanol (1) + PEG400 (2) system at two temperatures: ○, 298.15 K; ×, 328.15 K; —, modified Flory–Huggins model (eq 7).

Table 2. Physical Properties of Methanol[a]

$\frac{T}{\text{K}}$	$\frac{10^5 V_s^*}{\text{m}^3\cdot\text{mol}^{-1}}$	$\frac{10^3 B}{\text{m}^3\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{kg}\cdot\text{m}^{-3}}$	$\frac{p^*}{\text{kPa}}$
298.15	4.075	−1.9229	786.373	16.956
308.15	4.124	−1.5317	776.894	27.960
318.15	4.176	−1.2410	767.303	44.550
328.15	4.230	−1.0222	757.573	68.791

[a] Taken from ref 10.

Experimental data on density ρ and ultrasonic velocity u of various methanol + PEG solutions determined at $T = (288.15$ to $328.15)$ K are given in Table 3.

The excess molar volumes, V_m^{ex}, and the isentropic compression, $K_{s,m}^{ex} = -(\partial V_m^{ex}/\partial P)_s$ were determined by the following expressions:

$$V_m^{ex} = \sum_{i=1}^{2} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) \tag{4}$$

$$K_{s,m}^{ex} = \sum_{i=1}^{2} x_i M_i \left[\frac{1}{(\rho u)^2} - \frac{1}{(\rho_i u_i)^2}\right] \tag{5}$$

where x is the mole fraction; M is the molar mass; and subscripts 1 and 2 stand for methanol and polymer, respectively. The values obtained for V_m^{ex} and $K_{s,m}^{ex}$ at different concentrations and temperatures are also reported in Table 3. A plot of V_m^{ex} and $K_{s,m}^{ex}$ values versus polymer mole fraction are shown respectively in Figures 2 and 3. These figures show that at different concentrations and working temperatures both the V_m^{ex} and $K_{s,m}^{ex}$ are negative and become more negative when temperature increases. The negative V_m^{ex} value can be explained in terms of positive contributions due to breaking of like interactions of the pure liquids and negative contributions due to the formation of unlike (polymer–solvent) interactions and also accommodation of small methanol molecules in the voids provided by the PEG (packing effect). The interaction between the hydrogen atom of the hydroxyl group of methanol and the oxygen atoms of the poly(ethylene glycol) as well as the packing effect are responsible for the negative V_m^{ex} values obtained for the PEG + methanol system. The excess molar volume values reported for methanol + triethylene glycol[17] and methanol + poly(ethylene glycol) dimethyl ether 250[18] are also negative at different temperatures, and in these systems V_m^{ex} values also become more negative when temperature increases. This behavior of variation of V_m^{ex} with temperature is similar to that of PEG 400 + methanol studied in this work. Valtz et al.[17] reported that such behavior may be explained by the packing effects that become more dominant and increase with temperature.

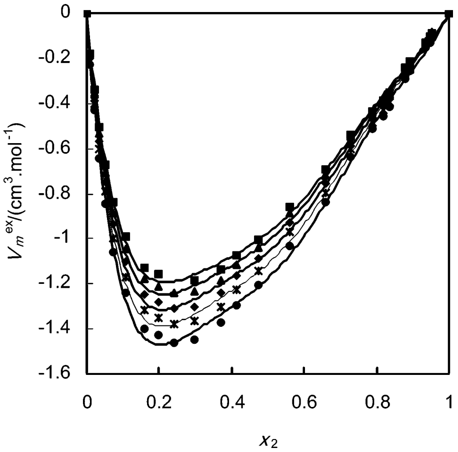

Figure 2. Plot of excess molar volume V_m^{ex}/(cm$^3\cdot$mol^{-1}) for methanol (1) + PEG400 (2) system against mole fraction of polymer x_2 at different temperatures: ■, 288.15 K; ▲, 298.15 K; ◆, 308.15 K; ×, 318.15 K; ●, 328.15 K. Lines were generated using the Redlich–Kister equation (eq 9).

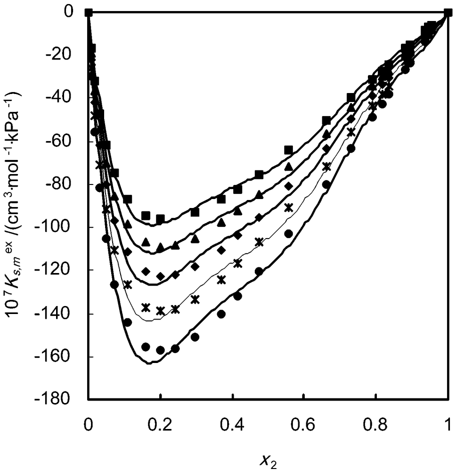

Figure 3. Plot of excess molar isentropic compression $K_{s,m}^{ex}$/(cm$^3\cdot$mol$^{-1}\cdot$kPa^{-1}) for methanol (1) + PEG400 (2) system against mole fraction of polymer x_2 at different temperatures: ■, 288.15 K; ▲, 298.15 K; ◆, 308.15 K; ×, 318.15 K; ●, 328.15 K. Lines were generated using the Redlich–Kister equation (eq 9).

The negative behavior reflected in Figure 3 for the excess molar isentropic compression for the whole range of composition and different temperatures implies a great difficulty to compress the PEG 400 + methanol solutions than the ideal behavior at different polymer mole fractions and the working temperatures. Figure 3 also shows that as the temperature increases, deviation of methanol + PEG400 solutions from the ideal behavior become larger.

Table 3. Experimental Densities ρ, Excess Molar Volumes V_m^{ex}, Ultrasonic Velocities u, and Excess Molar Isentropic Compression $K_{s,m}^{ex}$ for Methanol (1) + PEG400 (2) System at Different Temperatures

x_2	ρ g·cm^{-3}	V_m^{ex} cm^3·mol^{-1}	u m·s^{-1}	$10^7K_{s,m}^{ex}$ cm^3·mol^{-1}·kPa^{-1}	x_2	ρ g·cm^{-3}	V_m^{ex} cm^3·mol^{-1}	u m·s^{-1}	$10^7K_{s,m}^{ex}$ cm^3·mol^{-1}·kPa^{-1}	x_2	ρ g·cm^{-3}	V_m^{ex} cm^3·mol^{-1}	u m·s^{-1}	$10^7K_{s,m}^{ex}$ cm^3·mol^{-1}·kPa^{-1}
T = 288.15 K														
0.0000	0.79626	0.000	1141.69	0.00	0.2970	1.06968	−1.186	1528.13	−93.40	0.8354	1.12521	−0.354	1618.50	−24.25
0.0091	0.82468	−0.180	1173.37	−16.99	0.3705	1.08483	−1.134	1552.78	−87.04	0.8807	1.12702	−0.243	1621.16	−16.73
0.0195	0.85229	−0.336	1206.27	−32.07	0.4143	1.09171	−1.074	1564.09	−82.27	0.8938	1.12753	−0.216	1622.11	−14.88
0.0331	0.88262	−0.507	1244.93	−47.53	0.4748	1.09963	−1.004	1577.06	−75.32	0.9370	1.12913	−0.129	1624.90	−8.53
0.0505	0.91388	−0.669	1287.29	−61.79	0.5591	1.10806	−0.857	1590.83	−64.19	0.9466	1.12946	−0.106	1625.20	−6.69
0.0736	0.94651	−0.841	1334.02	−75.08	0.6601	1.11583	−0.694	1603.52	−50.41	0.9523	1.12964	−0.089	1625.52	−5.78
0.1077	0.98182	−0.992	1387.43	−86.58	0.7293	1.11990	−0.537	1609.89	−39.72	1.0000	1.13124	0.000	1629.13	0.00
0.1586	1.01786	−1.126	1444.13	−94.63	0.7903	1.12311	−0.433	1615.17	−30.98					
0.1998	1.03806	−1.159	1476.65	−96.29	0.8173	1.12441	−0.390	1617.38	−27.20					
T = 298.15 K														
0.0000	0.78683	0.000	1108.55	0.00	0.2427	1.04575	−1.243	1470.09	−108.03	0.8173	1.11617	−0.393	1583.06	−29.89
0.0091	0.81533	−0.189	1140.27	−19.27	0.2970	1.06121	−1.234	1495.18	−104.92	0.8354	1.11700	−0.362	1584.55	−27.16
0.0195	0.84305	−0.355	1173.79	−36.75	0.3705	1.07645	−1.181	1519.87	−97.94	0.8807	1.11880	−0.242	1586.75	−18.13
0.0331	0.87349	−0.535	1212.39	−54.10	0.4143	1.08333	−1.114	1530.74	−92.24	0.8938	1.11935	−0.224	1588.16	−16.81
0.0505	0.90485	−0.704	1255.34	−70.44	0.4748	1.09130	−1.041	1543.73	−84.55	0.9370	1.12092	−0.122	1590.40	−8.85
0.0736	0.93763	−0.886	1301.84	−85.16	0.5591	1.09975	−0.884	1557.03	−71.71	0.9466	1.12129	−0.110	1591.13	−7.53
0.1077	0.97310	−1.045	1355.64	−98.22	0.6601	1.10760	−0.723	1569.74	−56.48	0.9523	1.12143	−0.080	1591.00	−5.75
0.1586	1.00924	−1.180	1411.77	−106.78	0.7293	1.11163	−0.546	1575.73	−44.05	1.0000	1.12308	0.000	1595.03	0.00
0.1998	1.02952	−1.214	1444.43	−108.71	0.7903	1.11490	−0.448	1581.23	−34.67					
T = 308.15 K														
0.0000	0.77730	0.000	1075.71	0.00	0.2427	1.03726	−1.308	1437.95	−121.89	0.8173	1.10794	−0.414	1549.68	−33.51
0.0091	0.80591	−0.200	1107.72	−22.12	0.2970	1.05279	−1.299	1463.05	−118.43	0.8354	1.10877	−0.380	1551.15	−30.41
0.0195	0.83374	−0.376	1141.47	−42.08	0.3705	1.06806	−1.239	1487.44	−110.35	0.8807	1.11057	−0.253	1553.25	−20.22
0.0331	0.86433	−0.568	1180.41	−61.91	0.4143	1.07496	−1.167	1498.04	−103.76	0.8938	1.11113	−0.236	1554.72	−18.83
0.0505	0.89581	−0.745	1223.62	−80.42	0.4748	1.08296	−1.090	1510.96	−95.11	0.9370	1.11271	−0.131	1556.90	−9.88
0.0736	0.92874	−0.938	1270.18	−96.91	0.5591	1.09145	−0.927	1524.01	−80.57	0.9466	1.11308	−0.118	1557.63	−8.39
0.1077	0.96434	−1.104	1324.06	−111.49	0.6601	1.09934	−0.758	1536.61	−63.46	0.9523	1.11322	−0.087	1557.45	−6.35
0.1586	1.00062	−1.245	1380.00	−120.84	0.7293	1.10339	−0.576	1542.46	−49.48	1.0000	1.11487	0.000	1561.58	0.00
0.1998	1.02097	−1.279	1412.49	−122.83	0.7903	1.10665	−0.467	1547.82	−38.76					
T = 318.15 K														
0.0000	0.76764	0.000	1043.28	0.00	0.2427	1.02877	−1.379	1406.35	−137.79	0.8173	1.09972	−0.431	1517.04	−37.86
0.0091	0.79639	−0.214	1075.75	−25.63	0.2970	1.04436	−1.367	1431.24	−133.69	0.8354	1.10056	−0.397	1518.41	−34.25
0.0195	0.82435	−0.401	1109.63	−48.36	0.3705	1.05969	−1.302	1455.35	−124.36	0.8807	1.10237	−0.265	1520.53	−22.95
0.0331	0.85509	−0.604	1148.89	−71.02	0.4143	1.06662	−1.228	1465.97	−117.04	0.8938	1.10293	−0.247	1521.92	−21.22
0.0505	0.88672	−0.793	1192.20	−91.89	0.4748	1.07464	−1.144	1478.69	−107.12	0.9370	1.10451	−0.134	1524.25	−11.48
0.0736	0.91980	−0.995	1239.00	−110.51	0.5591	1.08316	−0.971	1491.68	−90.82	0.9466	1.10488	−0.120	1524.73	−9.37
0.1077	0.95555	−1.169	1292.80	−126.66	0.6601	1.09109	−0.794	1504.03	−71.38	0.9523	1.10502	−0.088	1524.67	−7.33
0.1586	0.99198	−1.315	1348.69	−136.95	0.7293	1.09515	−0.602	1509.81	−55.71	1.0000	1.10669	0.000	1528.71	0.00
0.1998	1.01242	−1.351	1380.97	−138.96	0.7903	1.09843	−0.488	1515.09	−43.59					
T = 328.15 K														
0.0000	0.75782	0.000	1011.15	0.00	0.2427	1.02030	−1.462	1375.30	−156.16	0.8173	1.09154	−0.459	1485.16	−43.03
0.0091	0.78676	−0.230	1043.98	−29.68	0.2970	1.03593	−1.445	1399.74	−151.00	0.8354	1.09236	−0.417	1486.20	−38.35
0.0195	0.81485	−0.429	1078.11	−55.74	0.3705	1.05132	−1.374	1423.71	−140.31	0.8807	1.09421	−0.288	1488.71	−26.53
0.0331	0.84576	−0.646	1117.80	−81.76	0.4143	1.05830	−1.298	1434.52	−132.33	0.8938	1.09474	−0.259	1489.68	−23.69
0.0505	0.87753	−0.844	1161.14	−105.23	0.4748	1.06634	−1.206	1446.87	−120.72	0.9370	1.09636	−0.151	1492.48	−13.76
0.0736	0.91082	−1.060	1208.29	−126.39	0.5591	1.07492	−1.029	1459.99	−102.66	0.9466	1.09671	−0.129	1492.45	−10.37
0.1077	0.94671	−1.240	1261.81	−144.10	0.6601	1.08285	−0.835	1471.97	−80.25	0.9523	1.09686	−0.098	1492.62	−8.58
0.1586	0.98334	−1.396	1317.88	−155.62	0.7293	1.08694	−0.637	1478.01	−63.16	1.0000	1.09852	0.000	1496.56	0.00
0.1998	1.00384	−1.430	1349.88	−157.48	0.7903	1.09023	−0.516	1482.93	−48.96					

Correlation of Data

Methanol activity values a_1 at each temperature reported in Table 1 were fitted to the original Flory−Huggins model,[19] which has the following form:

$$\ln a_1 = \ln z + \left(1 - \frac{1}{r_2}\right)(1 - z) + \chi_{12}(1 - z)^2 \qquad (6)$$

In eq 6, z is volume fraction of solvent, χ_{12} is the Flory parameter, and r_2 is the number of segments of polymer defined as the molar volume of polymer divided by the molar volume of solvent.

The result of fitting to the eq 6 is given in Table 4. The standard deviations σ (a_1) given in Table 4 indicates that the eq 6 represent the experimental methanol activity data fairly well. The χ_{12} value reported in Table 4 decreases as the temperature increases. This decreasing of the χ_{12} value indicates that as the temperature increases the interaction between PEG and methanol becomes stronger. However, since there is a little difference between the obtained χ_{12} values, the temperature has only small effect on the interaction between PEG and methanol.

The dependence of the Flory parameter on concentration and temperature, however, should be considered. The following modified Flory−Huggins equation

$$\ln a_1 = \ln z + \left(1 - \frac{1}{r_2}\right)(1 - z) + \left[\frac{d_0}{1 - f(1 - z)} + \frac{d_1}{T[1 - f(1 - z)]} + \frac{d_2 \ln T}{1 - f(1 - z)}\right](1 - z)^2 \qquad (7)$$

given by Bae et al.[20] was known to be the successful in representing the concentration as well as temperature dependency of the solvent activity data in binary polymer + solvent systems. Therefore, we also fitted the experimental methanol activity data of Table 1 to eq 7. The obtained parameters d_0, d_1, d_2, f, and standard deviation $\sigma(a_1)$ are respectively 167.919,

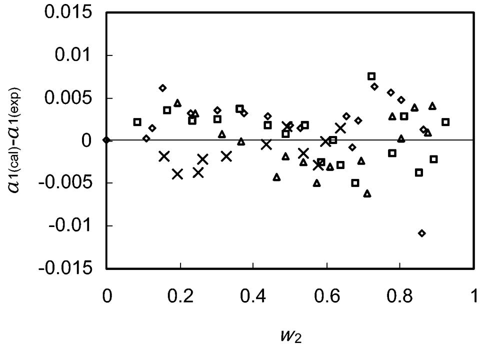

Figure 4. Difference between the experimental and calculated methanol activities with the modified Flory−Huggins model (eq 7) at different temperatures: ◇, 298.15 K; □, 308.15 K; △, 318.15 K; ×, 328.15 K.

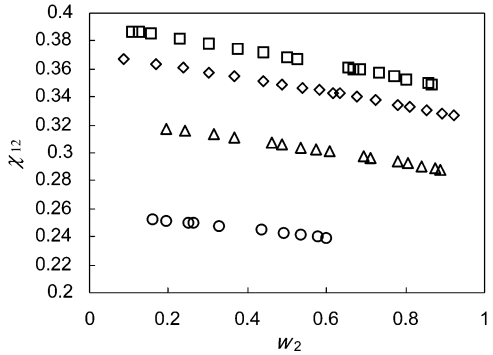

Figure 5. Variation of the Flory parameter χ_{12} with concentration and temperature for methanol (1) + PEG400 (2) system: □, 298.15 K; ◇, 308.15 K: △, 318.15 K: ○, 328.15 K.

Table 4. Flory Parameters Calculated from Equation 6 along with the Standard Deviations for Methanol Activity σ (a_1) for the System Methanol (1) + PEG400 (2) at Different Temperatures

T/K	χ_{12}	$\sigma(a_1)$
298.15	0.3522	0.0036
308.15	0.3290	0.0033
318.15	0.2815	0.0046
328.15	0.2329	0.0024

Table 5. Parameters of Equation 9 for V_m^{ex} along with the Corresponding Standard Deviations, $\sigma(V_m^{ex})$ for Methanol (1) + PEG400 (2) System at Different Temperatures

T						$\sigma(V_m^{ex})$
K	B_0	B_1	B_2	B_3	B_4	$cm^3 \cdot mol^{-1}$
288.15	−3.707	−2.630	−4.229	−4.339	-	0.04
	−3.900	−2.491	−1.262	−4.525	−4.713	0.02
298.15	−3.832	−2.642	−4.405	−4.844	-	0.04
	−4.042	−2.606	−1.363	−4.902	−4.909	0.02
308.15	−4.011	−2.768	−4.712	−5.171	-	0.04
	−4.236	−2.729	−1.452	−5.233	−5.260	0.03
318.15	−4.206	−2.917	−5.021	−5.558	-	0.05
	−4.446	−2.875	−1.545	−5.624	−5.609	0.03
328.15	−4.434	−3.086	−5.405	−5.911	-	0.05
	−4.700	−3.040	−1.552	−5.984	−6.216	0.03

−7394.856, −25.050, −0.147, and 0.0037. To see the performance of eq 7 in representing solvent activity data, the lines generated for methanol activity at (298.15 and 328.15) K were obtained using the parameters of eq 7, and these are also shown in Figure 1. The difference between the experimental and calculated methanol activities with the modified Flory−Huggins model (eq 7) are shown at different temperatures in Figure 4.

Table 6. Parameters of Equation 9 for $K_{s,m}^{ex}$ along with the Corresponding Standard Deviations $\sigma(K_{s,m}^{ex})$ for Methanol (1) + PEG400 (2) System at Different Temperatures

T						$10^7\sigma(K_{s,m}^{ex})$
K	B_0	B_1	B_2	B_3	B_4	$cm^3 \cdot mol^{-1} \cdot kPa^{-1}$
288.15	−273.96	205.18	−414.22	474.08		4.13
	−294.94	190.10	−92.32	494.24	−511.38	2.35
298.15	−305.72	217.62	−465.52	563.73		4.82
	−330.66	213.30	−104.16	570.57	−583.10	2.71
308.15	−343.28	243.86	−532.16	649.67		5.61
	−372.24	238.85	−112.58	657.61	−677.05	3.17
318.15	−385.90	273.21	−611.30	747.59		6.58
	−419.85	267.33	−119.41	756.90	−793.74	3.71
328.15	−434.33	306.18	−704.84	862.53		7.74
	−474.34	299.24	−125.07	873.51	−935.54	4.35

In the modified Flory−Huggins model, the Flory parameter χ_{12} is defined as

$$\chi_{12}(T, z) = \frac{d_0}{1 - f(1 - z)} + \frac{d_1}{T[1 - f(1 - z)]} + \frac{d_2 \ln T}{1 - f(1 - z)} \tag{8}$$

The variations of the Flory parameter χ_{12} with PEG mass fraction and the temperature were obtained from eq 8, and the corresponding plot is shown in Figure 5. Figure 5 shows that the modified Flory−Huggins model gives the χ_{12} values, which decrease by increase in temperature, similar to the trend obtained by the original Flory−Huggins model as reported in Table 4.

The excess molar volumes and the excess molar isentropic compressions were correlated by means of the Redlich−Kister equation:[21]

$$\Delta Q = x_2(1 - x_2)\sum_{p=0}^{N} B_p(2x_2 - 1)^p \tag{9}$$

where B_p represents the fitting coefficients and N is the degree of the polynomial expansion. The standard deviations, σ, between the calculated, ΔQ_{calc}, and the experimental, ΔQ_{exptl}, values have been estimated by using

$$\sigma = \left(\frac{\sum_{i=1}^{n_{DAT}} (\Delta Q_{exptl} - \Delta Q_{calc})^2}{n_{DAT}}\right)^{1/2} \tag{10}$$

where n_{DAT} is the number of experimental points. The obtained adjustable parameters, B_p, are summarized in Tables 5 and 6 together with the standard deviations, σ. Using eq 9 with $N = 4$ and the corresponding parameters for V_m^{ex} and $K_{s,m}^{ex}$ reported

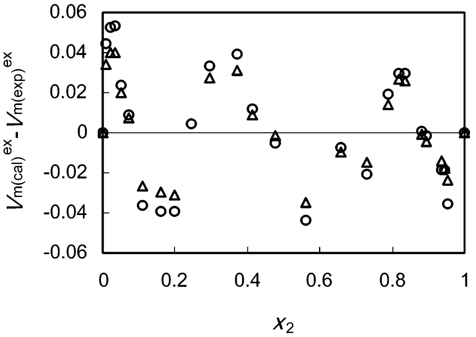

Figure 6. Difference between the experimental and calculated excess molar volumes V_m^{ex}, with the Redlich−Kister equation (eq 9) at two temperatures: △, 288.15 K; ○, 328.15 K.

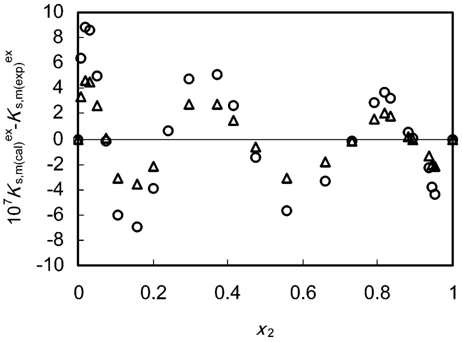

Figure 7. Difference between the experimental and calculated excess molar isentropic compression $K_{s,m}^{ex}$, with the Redlich−Kister equation (eq 9) at two temperatures: △, 288.15 K; ○, 328.15 K.

in Tables 5 and 6, the lines generated for V_m^{ex} and $K_{s,m}^{ex}$ were obtained, and these were also respectively shown in Figures 2 and 3 for the five studied isotherms. Slightly higher standard deviations for V_m^{ex} and $K_{s,m}^{ex}$ are obtained when we use eq 9 with $N = 3$, as can be seen in Tables 5 and 6. The difference between the experimental and calculated excess molar volumes and excess molar isentropic compressions with the Redlich−Kister equation (eq 9) are shown respectively in Figures 6 and 7 at two temperatures (288.15 and 328.15) K as examples. From the $K_{s,m}^{ex}$ values calculated from eq 9, one can easily evaluate the values for isentropic compressibility and speed of sound at a desired concentration with reasonable accuracy.

Conclusions

Accurate methanol activity data were determined for the methanol + PEG400 system at $T = (298.15$ to $328.15)$ K, and these data were fitted to the Flory−Huggins model. It was found that both the methanol activity and the Flory parameter decrease as the temperature is increased, indicating an increase of interaction between polymer and methanol by increasing the temperature. From the measured density and speed of sound data at $T = (288.15$ to $328.15)$ K, the values for excess molar volume and excess molar isentropic compression for methanol + PEG400 were calculated. Both of these quantities are negative at different concentrations and working temperatures. The negative excess molar volume along with the variation of the Flory parameter with temperature were used to obtain some information with regard to the polymer−solvent interactions and the packing effect. The negative excess molar isentropic compression values imply a greater difficulty to compress the methanol + PEG400 solutions than the ideal behavior at different temperatures considered in this work.

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