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

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Solvent activity measurements have been performed on the system poly(ethylene glycol) 400 (PEG400) + ethanol at $T = (298.15 \text{ to } 328.15)$ K using an improved isopiestic method. The solvent activity data were correlated with the original and modified Flory–Huggins models. The density, speed of sound, and viscosity data were also measured at $T = (288.15 \text{ to } 328.15)$ K for the PEG400 + ethanol system. From these experimental data, the excess molar volume, V^E, excess molar isentropic compression, $K^E_{s,m}$, and viscosity deviation, $\Delta\eta$, have been determined for each composition and fitted to the Redlich–Kister equation.

Introduction

Studies on thermodynamic and transport properties are important in understanding the nature of molecular interactions in binary liquid mixtures. Properties of mixtures are useful for designing many types of transport and process equipment in the chemical industry[1,2] and the theoretical interest in studying the structure of such solutions. Correlations between molecular weight and physical properties of polymers have been largely investigated, mostly in the high molecular weight range, while studies on low molecular weight polymers are less frequent. Nevertheless, several industrial applications make use of such substances, such as poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), and their copolymers. Because of their low toxicity, PEGs are frequently used in the pharmaceutical and cosmetic fields as solvents, carriers, humectants, lubricants, binders, bases, and coupling agents[3] and also for extraction, separation, and purification of biological materials.[4,5]

The vapor–liquid data have been compiled by Wohlfarth[6] for some polymer + solvent systems. Recently, with regard to PEG + alcohol solutions, a few vapor pressure data for PEG + methanol and PEG + ethanol systems with polymers of molar mass of 600 have been measured[7] at 303.15 K by an apparatus based on the principle of electromicrobalance. In their vapor sorption measurements,[7] 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 pressures or activity data for PEG + 2-propanol[8] with different molar masses of PEG and PEG400 + methanol.[9] However, as far as we know, there are no vapor pressure or activity data for the PEG400 + ethanol system at different temperatures. In this work, solvent activity data for PEG400 + ethanol were measured at $T = (298.15 \text{ to } 328.15)$ K using an improved isopiestic method. The recent vapor pressure measurements on the solutions of LiBr in ethanol[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 ethanol systems as an isopiestic standard, and therefore isopiestic measurement is now possible at higher concentrations and temperatures for solutions of other salts or polymers in ethanol than was possible before.

Although some work has been conducted on the characterization of water solutions of PEGs with different molar masses, few data are reported in the literature on mixtures of PEGs with organic solvents.

In this work, density, ρ, speed of sound, u, and viscosity, η, were also measured for the system PEG400 + ethanol under atmospheric pressure at $T = (288.15 \text{ to } 328.15)$ K, from which the values for the excess molar volume, V^E, excess molar isentropic compression, $K^E_{s,m}$, and viscosity deviation, $\Delta\eta$, were calculated, and the results were fitted to the Redlich–Kister equation. For the system PEG400 + ethanol, there is no density, speed of sound, or viscosity data at different temperatures in the literature. Only recently, a few density and viscosity data of PEG300 + ethanol at $T = (308.2, 318.2, 328.2, \text{ and } 338.2)$ K were published.[11] Also, Aminabhavi et al.[12] have reported density, viscosity, and speed of sound data for PEG400 + methyl acetate in the temperature interval (298.15 to 308.15) K. Recently, the density and viscosity of PEG + 2-methyltetrahydrofuran has been measured at $T = (293.15, 303.15, \text{ and } 313.15)$ K by Francesconi et al.[13] with polymers of relative molar masses of 200 and 400.

The variation of activity, excess molar volume, and excess molar isentropic compression values with the polymer concentration and temperature provide us useful information with regard to polymer–solvent interactions and deviation of polymer solution from ideal solution.

Experimental Procedure

Materials. All the chemicals were obtained from Merck. Lithium bromide with a purity of minimum mass fraction of 0.995 was dried in an electric oven at about 110 °C for 24 h prior to use. Ethanol with a purity of minimum mass fraction of 0.995 was dehydrated according to Vogel.[14] Double distilled, deionized water was used. For the molar mass of PEG, the value 400 $\text{g} \cdot \text{mol}^{-1}$ was used.

Apparatus and Procedures. The isopiestic apparatus employed is essentially similar to the one used previously.[15]

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Recently, this technique has been used for the measurement of activity of the methanol in alcohol + poly(vinylpyrrolidone),[16] alcohol + poly(propylene glycol),[17] and 2-propanol in 2-propanol + poly(ethylene glycol)[8] 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 an ethanol reservoir. The apparatus was held in a constant temperature bath at least 120 h for equilibration at $T = (298.15 \text{ to } 328.18)$ K. The temperature was controlled to within ± 0.005 °C by a Heto temperature controller (Hetotherm PF, Heto Laboratory 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 $\pm 1 \cdot 10^{-7}$ 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 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 PEG400 + ethanol 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).[18] 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.[19] The uncertainty of the instrument is $\pm 0.003 \text{ kg} \cdot \text{m}^{-3}$ for density and $\pm 0.5 \text{ m} \cdot \text{s}^{-1}$ for ultrasonic velocity.

In this work, the viscosities of the polymer solutions were determined using a suspended Ubbelohde-type viscometer (Julabo, MD-18V, Germany) at $T = (288.15 \text{ to } 328.15)$ K in which the temperature was controlled with a precision of 0.01 K. The flow times were measured using a stopwatch. The precision of the used stopwatch was ± 0.01 s. The dynamic viscosity, η, was calculated by the following relation

$$\eta = \rho K(t - \theta) \tag{1}$$

where t is the flow time; K is the viscometer constant; θ is the Hagenbach correction factor; and ρ is the density. The viscometer constant, K, is determined by calibrating at working temperatures with distilled water using viscosity values from the literature.[20] The uncertainty for the dynamic viscosity determination was estimated to be ± 0.5 %. Each measurement was repeated five times.

Density, speed of sound, and viscosity values of the pure components are given in Table 1 at different temperatures and compared with the literature values.

Table 1. Density, ρ, Speed of Sound, u, and Dynamic Viscosity, η, for Pure Components at $T = (288.15 \text{ to } 328.15)$ K

component	T / K	ρ / $\text{g} \cdot \text{cm}^{-3}$	u / $\text{m} \cdot \text{s}^{-1}$	η / $\text{mPa} \cdot \text{s}$
ethanol	288.15	0.79363	1177.25	1.30
	298.15	0.78506	1142.97	1.07
		0.785085[31]	1143.10[31]	1.084[32]
		0.78522[33]		1.077[33]
		0.78504[34]		
	308.15	0.77640	1109.19	0.89
		0.77551[32]	1111[32]	0.903[32]
		0.77726[35]		
	318.15	0.76758	1075.84	0.75
	328.15	0.75858	1042.77	0.63
poly(ethylene glycol) (PEG400)	288.15	1.13129	1627.33	150.64
	298.15	1.12310	1593.01	84.71
		1.12230[36]		
	308.15	1.11489	1559.50	51.66
	318.15	1.10671	1526.61	33.81
	328.15	1.09854	1494.34	23.36

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 ethanol as reported in Table 2 enabled the calculation of the solvent activity, a_1, in the solutions of ethanol (1) + PEG (2) from that of reference solutions using the relations

$$\ln a_1 = -\upsilon m_{\text{LiBr}} \varphi_{\text{LiBr}} M_{\text{S}}, \quad m_{\text{LiBr}} = \frac{w_{\text{LiBr}}}{M_{\text{LiBr}}(1 - w_{\text{LiBr}})} \tag{2a,b}$$

where υ is the sum of stoichiometric numbers of the 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 the Archer equation[21,22]

$$\varphi_{\text{LiBr}} = \left[1 - A_{\varphi}\left(\frac{\sqrt{m_{\text{LiBr}}}}{1 + b\sqrt{m_{\text{LiBr}}}}\right)\right] + m_{\text{LiBr}}\left(\beta^{(0)} + \beta^{(1)}\exp[-\alpha_1\sqrt{m_{\text{LiBr}}}] + \beta^{(2)}\exp[-\alpha_2\sqrt{m_{\text{LiBr}}}]\right) + (m_{\text{LiBr}})^2\left(C^{(0)} + C^{(1)}\exp[-\alpha_3\sqrt{I}]\right) \tag{3}$$

The parameters of eq 3 for LiBr in ethanol solutions in the concentration range $(0.0705 \text{ to } 3.4451) \text{ mol} \cdot \text{kg}^{-1}$ and the temperature range of $T = (298.15 \text{ to } 333.15)$ 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 a standard deviation of about 0.01 in the above concentration and temperature ranges. The obtained ethanol activity data for the system ethanol (1) + PEG400 (2) are given in Table 2. To see the effect of temperature on the ethanol 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 ethanol solutions, p, were determined with the help of the following relation

$$\ln(a_1) = \ln\left(\frac{p}{p^*}\right) + \frac{(B - V_{\text{s}}^*)(p - p^*)}{RT} \tag{4}$$

where B, V^*_{s}, and p^* are the second virial coefficient, molar volume, and vapor pressure of pure ethanol, respectively. The

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

w_{LiBr}	w_2	Φ_{LiBr}	a_1	p/kPa
		T = 298.15 K		
0.0000	0.0000	1.000	1.0000	7.874
0.0143	0.0962	0.759	0.9884	7.783
0.0203	0.1202	0.753	0.9836	7.745
0.0266	0.1639	0.753	0.9784	7.704
0.0395	0.2274	0.763	0.9673	7.616
0.0411	0.2369	0.765	0.9659	7.605
0.0481	0.2745	0.776	0.9593	7.553
0.0593	0.3264	0.799	0.9480	7.465
0.0630	0.3460	0.808	0.9439	7.432
0.0656	0.3587	0.815	0.9411	7.410
0.0704	0.3778	0.829	0.9356	7.367
0.0840	0.4373	0.874	0.9185	7.232
0.0867	0.4521	0.884	0.9149	7.204
0.0989	0.4974	0.936	0.8967	7.060
0.1008	0.5092	0.945	0.8937	7.037
0.1117	0.5497	0.999	0.8753	6.892
0.1230	0.5893	1.065	0.8536	6.721
0.1397	0.6435	1.179	0.8163	6.427
0.1467	0.6712	1.234	0.7985	6.288
0.1560	0.6941	1.312	0.7732	6.088
0.1915	0.7869	1.685	0.6547	5.155
0.2164	0.8403	2.025	0.5524	4.350
		T = 308.15 K		
0.0000	0.0000	1.000	1.0000	13.751
0.0175	0.1061	0.722	0.9864	13.564
0.0219	0.1218	0.725	0.9829	13.516
0.0234	0.1325	0.726	0.9816	13.498
0.0380	0.2018	0.748	0.9691	13.327
0.0455	0.2379	0.762	0.9622	13.231
0.0567	0.2935	0.788	0.9509	13.076
0.0653	0.3386	0.811	0.9417	12.949
0.0688	0.3513	0.821	0.9377	12.894
0.0767	0.3839	0.846	0.9282	12.763
0.0793	0.3967	0.855	0.9248	12.717
0.0980	0.4718	0.930	0.8983	12.353
0.1016	0.4827	0.946	0.8927	12.275
0.1150	0.5411	1.015	0.8695	11.956
0.1355	0.6090	1.141	0.8273	11.376
0.1519	0.6607	1.266	0.7862	10.811
0.1546	0.6726	1.289	0.7786	10.707
0.1665	0.7039	1.395	0.7440	10.230
0.1893	0.7643	1.635	0.6670	9.172
		T = 318.15 K		
0.0000	0.0000	1.000	1.0000	23.042
0.0198	0.1117	0.714	0.9848	22.692
0.0285	0.1688	0.724	0.9777	22.528
0.0304	0.1776	0.727	0.9761	22.491
0.0557	0.2859	0.777	0.9525	21.947
0.0664	0.3313	0.806	0.9409	21.680
0.0983	0.4436	0.920	0.8991	20.717
0.1157	0.5042	1.005	0.8698	20.043
0.1446	0.5975	1.187	0.8082	18.622
0.1607	0.6431	1.314	0.7658	17.646
0.1675	0.6618	1.375	0.7455	17.179
0.1825	0.7086	1.522	0.6973	16.068
		T = 328.15 K		
0.0000	0.0000	1.000	1.0000	37.301
0.0248	0.1405	0.708	0.9811	36.595
0.0412	0.1981	0.734	0.9671	36.074
0.0516	0.2405	0.756	0.9573	35.708
0.0688	0.3175	0.801	0.9392	35.032
0.0731	0.3346	0.814	0.9342	34.846
0.0758	0.3420	0.822	0.9309	34.725
0.0893	0.3952	0.870	0.9135	34.073
0.0993	0.4352	0.911	0.8989	33.529
0.0997	0.4404	0.913	0.8983	33.507
0.1165	0.4916	0.994	0.8702	32.458
0.1739	0.6748	1.408	0.7303	27.239
0.2146	0.7809	1.865	0.5824	21.722

values of the physical properties for ethanol are summarized in Table 3. The experimental vapor pressure data are also given in Table 2.

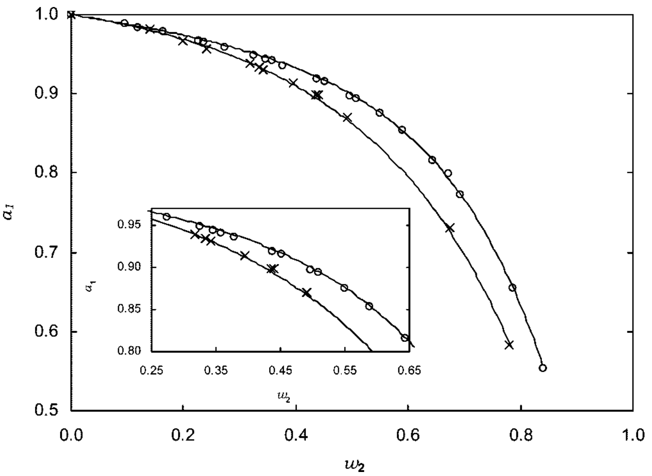

Figure 1. Experimental and calculated activity of ethanol a_1, plotted against mass fraction of polymer, w_2, for the ethanol (1) + PEG400 (2) system at two temperatures: ○, 298.15 K; ×, 328.15 K; —, modified Flory–Huggins model (eq 10).

Table 3. Physical Properties of Ethanol

T/K	$10^5 V^*_s$[a]/($\mathrm{m^3 \cdot mol^{-1}}$)	$10^3 B$[b]/($\mathrm{m^3 \cdot mol^{-1}}$)	p^*[c]/kPa
298.15	5.869	−2.8357	7.874
308.15	5.935	−2.2570	13.751
318.15	6.005	−1.8259	23.042
328.15	6.078	−1.5007	37.301

[a] Taken from ref 37. [b] Taken from ref 38. [c] Taken from ref 10.

Experimental data on density ρ and ultrasonic velocity u of various ethanol + PEG solutions determined at T = (288.15 to 328.15) K are given in Table 4.

The excess molar volumes V^E and the isentropic compression $K^E_{s,m} = -(\partial V^E/\partial P)_s$ were determined by the following expressions[23]

$$V^E = \sum_{i=1}^{2} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) \tag{5}$$

$$K^E_{s,m} = \sum_{i=1}^{2} x_i M_i \left(\frac{1}{(\rho u)^2} - \frac{1}{(\rho_i u_i)^2}\right) \tag{6}$$

where x is the mole fraction; M is the molar mass; and subscripts 1 and 2 stand for ethanol and polymer, respectively. The values obtained for V^E and $K^E_{s,m}$ at different concentrations and temperatures are also reported in Table 4. Plots of V^E and $K^E_{s,m}$ 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^E and $K^E_{s,m}$ are negative and become more negative with an increase in temperature. The negative V^E 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 ethanol molecules in the voids provided by the PEG (packing effect). The interaction between the hydrogen atom of the hydroxyl group of ethanol and the oxygen atoms of the poly(ethylene glycol), as well as the packing effect, might be responsible for the negative V^E values obtained for the PEG + ethanol system. The excess molar volume values reported for PEG + cyclic ethers at 303.15 K[24] with polymers of relative

Table 4. Experimental Densities ρ, Excess Molar Volumes V^E, Ultrasonic Velocities u, and Excess Molar Isentropic Compression $K^E_{s,m}$ for the Ethanol (1) + PEG400 (2) System at Different Temperatures

x_2	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})	u (m·s^{-1})	$10^7K^E_{s,m}$ (cm^3·mol^{-1}·kPa^{-1})	x_2	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})	u (m·s^{-1})	$10^7K^E_{s,m}$ (cm^3·mol^{-1}·kPa^{-1})
T = 288.15 K									
0.0000	0.79363	0.000	1177.25	0.0	0.3778	1.06475	−0.834	1526.56	−99.6
0.0012	0.79623	−0.015	1180.17	−2.1	0.4575	1.08071	−0.781	1550.39	−92.5
0.0023	0.79876	−0.031	1182.81	−4.0	0.5047	1.08838	−0.739	1562.20	−87.7
0.0034	0.80122	−0.045	1185.38	−5.8	0.5669	1.09690	−0.655	1574.76	−79.8
0.0046	0.80361	−0.056	1187.81	−7.4	0.6442	1.10583	−0.579	1588.99	−70.7
0.0057	0.80609	−0.076	1190.49	−9.3	0.7382	1.11446	−0.427	1601.67	−56.7
0.0069	0.80842	−0.080	1192.90	−10.7	0.7462	1.11511	−0.414	1602.67	−55.5
0.0080	0.81068	−0.093	1195.31	−12.3	0.7971	1.11916	−0.366	1608.37	−47.8
0.0091	0.81303	−0.107	1197.79	−14.0	0.8558	1.12306	−0.235	1615.43	−39.8
0.0103	0.81527	−0.116	1200.16	−15.4	0.8507	1.12270	−0.234	1614.31	−39.7
0.0114	0.81754	−0.131	1202.64	−17.1	0.8742	1.12431	−0.225	1617.19	−37.0
0.0129	0.82044	−0.146	1205.62	−18.9	0.8897	1.12521	−0.185	1617.84	−33.4
0.0279	0.84771	−0.291	1235.71	−36.4	0.9182	1.12688	−0.131	1621.16	−29.9
0.0469	0.87679	−0.421	1269.32	−52.8	0.9132	1.12652	−0.119	1621.11	−31.1
0.0710	0.90782	−0.589	1307.17	−69.3	0.9317	1.12763	−0.103	1621.47	−26.6
0.1026	0.93966	−0.682	1348.41	−82.8	0.9382	1.12799	−0.091	1622.91	−26.8
0.1475	0.97456	−0.784	1395.77	−94.9	0.9521	1.12875	−0.067	1623.94	−24.4
0.2129	1.01113	−0.870	1447.75	−103.2	0.9647	1.12940	−0.038	1625.06	−22.5
0.2642	1.03243	−0.920	1478.67	−105.2	0.9748	1.12995	−0.025	1625.22	−20.0
0.3162	1.04923	−0.913	1503.17	−103.8	1.0000	1.13129	0.000	1627.33	−16.3
T = 298.15 K									
0.0000	0.78506	0.000	1142.97	0.0	0.3778	1.05648	−0.880	1493.80	−112.3
0.0012	0.78769	−0.018	1146.25	−2.8	0.4575	1.07241	−0.814	1517.07	−103.7
0.0023	0.79021	−0.034	1148.61	−4.6	0.5047	1.08010	−0.772	1528.87	−98.3
0.0034	0.79269	−0.050	1151.46	−6.9	0.5669	1.08862	−0.681	1541.12	−89.0
0.0046	0.79506	−0.060	1153.64	−8.4	0.6442	1.09758	−0.602	1555.38	−78.9
0.0057	0.79757	−0.083	1156.67	−11.0	0.7382	1.10621	−0.439	1567.59	−62.5
0.0069	0.79988	−0.087	1158.82	−12.3	0.7462	1.10690	−0.435	1568.87	−61.7
0.0080	0.80217	−0.102	1161.56	−14.5	0.7971	1.11092	−0.375	1574.17	−52.4
0.0091	0.80450	−0.115	1163.80	−16.1	0.8558	1.11486	−0.247	1581.41	−43.7
0.0103	0.80676	−0.126	1166.54	−18.1	0.8507	1.11452	−0.253	1580.26	−43.6
0.0114	0.80901	−0.141	1168.72	−19.6	0.8742	1.11609	−0.230	1582.82	−40.1
0.0129	0.81194	−0.159	1172.16	−22.1	0.8897	1.11699	−0.188	1583.46	−36.1
0.0279	0.83921	−0.310	1202.37	−41.8	0.9182	1.11868	−0.137	1586.67	−32.0
0.0469	0.86833	−0.450	1236.80	−61.0	0.9132	1.11836	−0.137	1587.30	−34.4
0.0710	0.89939	−0.626	1274.65	−79.3	0.9317	1.11947	−0.119	1587.46	−29.1
0.1026	0.93127	−0.725	1316.57	−95.0	0.9382	1.11978	−0.091	1588.41	−28.4
0.1475	0.96619	−0.831	1363.55	−108.0	0.9521	1.12057	−0.075	1589.90	−26.5
0.2129	1.00280	−0.920	1415.56	−117.1	0.9647	1.12122	−0.045	1590.96	−24.2
0.2642	1.02413	−0.971	1446.41	−119.1	0.9748	1.12174	−0.021	1590.64	−20.6
0.3162	1.04090	−0.956	1470.39	−117.0	1.0000	1.12310	0.000	1593.01	−16.9
T = 308.15 K									
0.0000	0.77640	0.000	1109.19	0.0	0.3778	1.04817	−0.929	1461.49	−126.7
0.0012	0.77903	−0.019	1112.53	−3.2	0.4575	1.06412	−0.858	1484.41	−116.7
0.0023	0.78156	−0.036	1114.93	−5.3	0.5047	1.07181	−0.810	1496.16	−110.5
0.0034	0.78404	−0.053	1117.84	−8.0	0.5669	1.08035	−0.716	1508.18	−99.8
0.0046	0.78641	−0.064	1120.01	−9.7	0.6442	1.08933	−0.633	1522.28	−88.2
0.0057	0.78892	−0.088	1123.14	−12.7	0.7382	1.09797	−0.461	1534.35	−69.7
0.0069	0.79123	−0.092	1125.28	−14.2	0.7462	1.09867	−0.459	1535.56	−68.6
0.0080	0.79353	−0.109	1128.12	−16.7	0.7971	1.10269	−0.393	1540.88	−58.3
0.0091	0.79586	−0.123	1130.35	−18.5	0.8558	1.10663	−0.258	1547.92	−48.1
0.0103	0.79812	−0.134	1133.16	−20.8	0.8507	1.10630	−0.267	1546.84	−48.2
0.0114	0.80038	−0.150	1135.34	−22.6	0.8742	1.10787	−0.242	1549.38	−44.1
0.0129	0.80331	−0.169	1138.88	−25.5	0.8897	1.10877	−0.198	1550.03	−39.7
0.0279	0.83063	−0.331	1169.49	−48.2	0.9182	1.11046	−0.144	1553.19	−35.0
0.0469	0.85980	−0.480	1204.44	−70.2	0.9132	1.11015	−0.146	1553.81	−37.6
0.0710	0.89068	−0.646	1242.36	−90.4	0.9317	1.11126	−0.127	1554.01	−31.8
0.1026	0.92283	−0.772	1284.75	−108.5	0.9382	1.11158	−0.101	1554.88	−30.9
0.1475	0.95778	−0.882	1331.78	−122.9	0.9521	1.11235	−0.078	1556.38	−28.8
0.2129	0.99443	−0.974	1383.70	−132.8	0.9647	1.11301	−0.048	1557.45	−26.3
0.2642	1.01579	−1.026	1414.31	−134.7	0.9748	1.11354	−0.027	1557.09	−22.2
0.3162	1.03228	−0.966	1438.05	−131.6	1.0000	1.11489	0.000	1559.50	−18.1
T = 318.15 K									
0.0000	0.76758	0.000	1075.84	0.0	0.3778	1.03986	−0.984	1429.50	−142.9
0.0012	0.77022	−0.020	1079.18	−3.6	0.4575	1.05583	−0.906	1452.34	−131.4
0.0023	0.77275	−0.038	1081.61	−6.1	0.5047	1.06354	−0.856	1463.89	−124.2
0.0034	0.77524	−0.057	1084.47	−9.0	0.5669	1.07209	−0.755	1475.92	−112.2
0.0046	0.77761	−0.068	1086.85	−11.2	0.6442	1.08109	−0.666	1489.87	−98.8
0.0057	0.78013	−0.094	1089.85	−14.5	0.7382	1.08974	−0.483	1501.83	−77.9
0.0069	0.78244	−0.098	1092.18	−16.4	0.7462	1.09046	−0.485	1502.99	−76.6
0.0080	0.78475	−0.117	1094.90	−19.1	0.7971	1.09448	−0.413	1508.27	−64.9

Table 4 Continued

x_2	ρ / (g·cm^{-3})	V^E / (cm^3·mol^{-1})	u / (m·s^{-1})	$10^7K^E_{s,m}$ / (cm^3·mol^{-1}·kPa^{-1})	x_2	ρ / (g·cm^{-3})	V^E / (cm^3·mol^{-1})	u / (m·s^{-1})	$10^7K^E_{s,m}$ / (cm^3·mol^{-1}·kPa^{-1})
				T = 318.15 K					
0.0091	0.78709	−0.132	1097.33	−21.4	0.8558	1.09843	−0.272	1515.20	−53.3
0.0103	0.78935	−0.144	1100.04	−23.9	0.8507	1.09809	−0.279	1514.10	−53.4
0.0114	0.79161	−0.161	1102.37	−26.1	0.8742	1.09966	−0.251	1516.69	−48.8
0.0129	0.79455	−0.181	1105.82	−29.3	0.8897	1.10057	−0.207	1517.37	−44.0
0.0279	0.82193	−0.354	1136.98	−55.5	0.9182	1.10226	−0.149	1520.46	−38.5
0.0469	0.85116	−0.514	1172.28	−80.6	0.9132	1.10196	−0.155	1520.96	−41.2
0.0710	0.88199	−0.679	1210.63	−103.5	0.9317	1.10306	−0.130	1521.24	−34.9
0.1026	0.91431	−0.824	1253.22	−124.0	0.9382	1.10338	−0.103	1522.12	−33.9
0.1475	0.94934	−0.942	1300.42	−140.1	0.9521	1.10416	−0.081	1523.52	−31.3
0.2129	0.98604	−1.036	1352.17	−150.7	0.9647	1.10482	−0.050	1524.59	−28.5
0.2642	1.00745	−1.091	1382.62	−152.5	0.9748	1.10535	−0.027	1524.35	−24.2
0.3162	1.02389	−1.016	1406.30	−148.7	1.0000	1.10671	0.000	1526.61	−19.3
				T = 328.15 K					
0.0000	0.75858	0.000	1042.77	0.0	0.3778	1.03154	−1.048	1397.92	−161.2
0.0012	0.76120	−0.020	1045.98	−3.9	0.4575	1.04757	−0.969	1420.93	−148.3
0.0023	0.76376	−0.041	1048.71	−7.1	0.5047	1.05527	−0.909	1432.03	−139.4
0.0034	0.76624	−0.059	1051.37	−10.2	0.5669	1.06387	−0.809	1444.32	−126.2
0.0046	0.76864	−0.074	1054.02	−13.1	0.6442	1.07286	−0.706	1457.88	−110.3
0.0057	0.77114	−0.098	1056.72	−16.3	0.7382	1.08152	−0.510	1470.09	−87.0
0.0069	0.77349	−0.107	1059.38	−19.0	0.7462	1.08225	−0.514	1470.91	−85.0
0.0080	0.77577	−0.123	1061.84	−21.7	0.7971	1.08629	−0.439	1476.44	−72.3
0.0091	0.77814	−0.142	1064.54	−24.7	0.8558	1.09024	−0.289	1483.01	−58.3
0.0103	0.78039	−0.153	1067.05	−27.3	0.8507	1.08990	−0.296	1481.93	−58.5
0.0114	0.78268	−0.174	1069.68	−30.2	0.8742	1.09146	−0.261	1484.81	−53.9
0.0129	0.78561	−0.194	1072.96	−33.5	0.8897	1.09241	−0.227	1485.56	−48.7
0.0279	0.81307	−0.380	1104.76	−64.0	0.9182	1.09410	−0.164	1488.52	−42.2
0.0469	0.84238	−0.551	1140.23	−92.5	0.9132	1.09378	−0.165	1488.74	−44.6
0.0710	0.87309	−0.709	1179.26	−118.6	0.9317	1.09488	−0.138	1489.47	−38.4
0.1026	0.90570	−0.881	1221.88	−141.8	0.9382	1.09521	−0.112	1490.23	−37.0
0.1475	0.94084	−1.010	1269.42	−160.0	0.9521	1.09598	−0.085	1491.22	−33.2
0.2129	0.97760	−1.106	1320.87	−171.0	0.9647	1.09665	−0.055	1492.30	−30.1
0.2642	0.99905	−1.160	1351.20	−172.6	0.9748	1.09721	−0.040	1492.59	−26.5
0.3162	1.01575	−1.116	1375.05	−168.7	1.0000	1.09854	0.000	1494.34	−19.7

molar masses of 200 and 400 and PEG400 + methanol[9] in the temperature interval (288.15 to 328.15) K are also negative at different temperatures, and in these systems V^E values also become more negative when temperature increases. This behavior of variation of V^E with temperature is thus similar to that of PEG400 + ethanol studied in this work. Valtz et al.[25] reported that such behavior may be explained by the packing effects which become more dominant and increase with temperature.

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

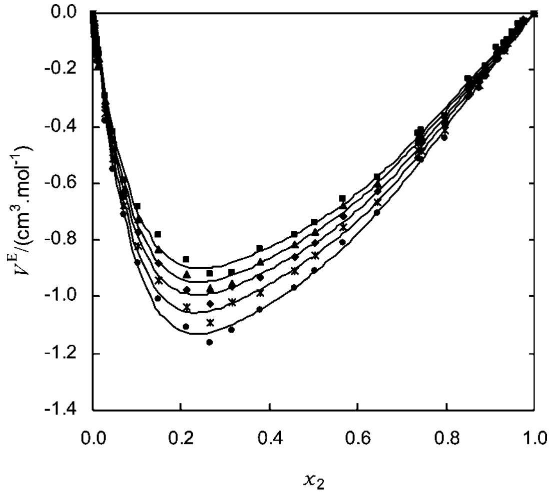

Figure 2. Plot of excess molar volume V^E/(cm^3·mol^{-1}) for the ethanol (1) + PEG400 (2) system against mole fraction of polymer x_2 at different temperatures: ■, 288.15 K; ▲, 298.15 K; ♦, 308.15 K; ×, 318.15 K; ●, 328.15 K. Lines were generated using the Redlich–Kister equation (eq 12).

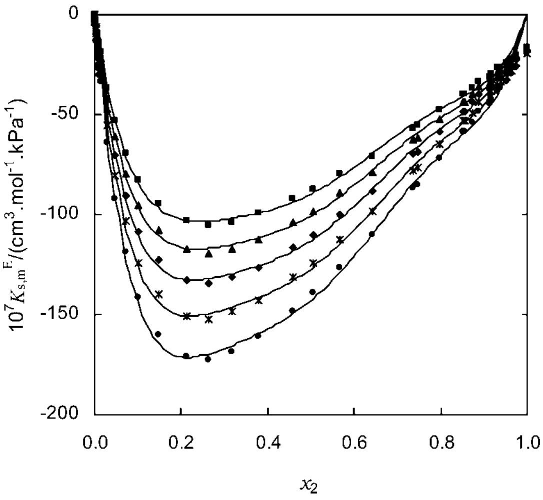

Figure 3. Plot of excess molar isentropic compression $K^E_{s,m}$/(cm^3·mol^{-1}·kPa^{-1}) for the ethanol (1) + PEG400 (2) system against mole fraction of polymer x_2 at different temperatures: ■, 288.15 K; ▲, 298.15 K; ♦, 308.15 K; ×, 318.15 K; ●, 328.15 K. Lines were generated using the Redlich–Kister equation (eq 12).

Table 5. Experimental Dynamic Viscosities, η, and Viscosity Deviations, $\Delta\eta$, for the Ethanol (1) + PEG400 (2) System at Different Temperatures

x_2	η (mPa·s)	$\Delta\eta$ (mPa·s)	x_2	η (mPa·s)	$\Delta\eta$ (mPa·s)
	T = 288.15 K			T = 318.15 K	
0.0000	1.30	0.00	0.0000	0.75	0.00
0.0999	6.57	−9.65	0.0999	3.12	−0.93
0.1998	14.01	−17.12	0.1998	6.26	−1.09
0.2997	25.73	−20.33	0.2997	8.92	−1.74
0.3997	40.95	−20.03	0.3997	12.68	−1.28
0.4996	57.36	−18.54	0.4996	16.48	−0.78
0.5997	75.37	−15.48	0.5997	20.28	−0.29
0.6994	94.14	−11.60	0.6994	23.88	0.01
0.7997	115.66	−5.06	0.7997	27.33	0.15
0.9001	133.44	−2.28	0.9001	30.73	0.23
1.0000	150.64	0.00	1.0000	33.81	0.00
	T = 298.15 K			T = 328.15 K	
0.0000	1.07	0.00	0.0000	0.63	0.00
0.0999	4.98	−4.44	0.0999	2.21	−0.70
0.1998	9.83	−7.95	0.1998	4.77	−0.40
0.2997	17.29	−8.85	0.2997	6.69	−0.75
0.3997	26.05	−8.45	0.3997	9.25	−0.46
0.4996	35.50	−7.35	0.4996	11.89	−0.09
0.5997	45.17	−6.06	0.5997	14.45	0.19
0.6994	55.48	−4.09	0.6994	16.98	0.45
0.7997	65.41	−2.54	0.7997	19.20	0.39
0.9001	75.14	−1.22	0.9001	21.34	0.26
1.0000	84.71	0.00	1.0000	23.36	0.00
	T = 308.15 K				
0.0000	0.89	0.00			
0.0999	3.89	−2.07			
0.1998	7.23	−3.80			
0.2997	12.13	−3.97			
0.3997	17.69	−3.49			
0.4996	23.52	−2.73			
0.5997	29.44	−1.90			
0.6994	35.34	−1.06			
0.7997	40.97	−0.52			
0.9001	46.48	−0.10			
1.0000	51.66	0.00			

Table 6. Interaction Parameters, ϵ, Calculated from Equation 8 for the System Ethanol (1) + PEG400 (2) at Different Temperatures

T/K	ϵ
288.15	6.049
298.15	5.645
308.15	5.357
318.15	5.189
328.15	4.915

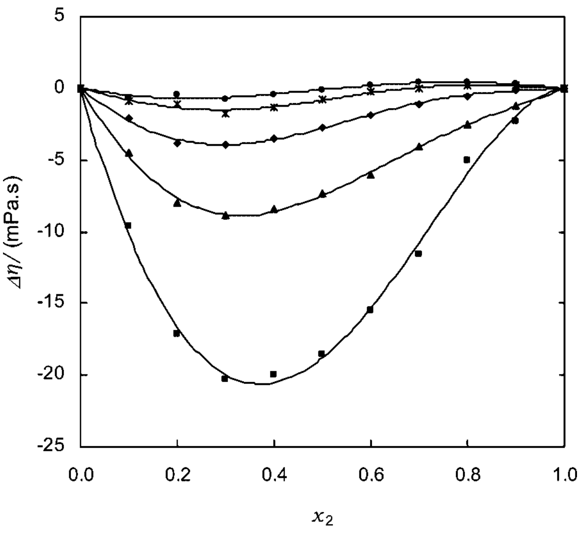

Figure 4. Plot of viscosity deviation $\Delta\eta$/(mPa·s) for the ethanol (1) + PEG400 (2) system against mole fraction of polymer x_2 at different temperatures: ■, 288.15 K; ▲, 298.15 K; ♦, 308.15 K; ×, 318.15 K; ●, 328.15 K. Lines were generated using the Redlich–Kister equation (eq 12).

Table 7. Flory Parameters Calculated from Equation 9 along with the Standard Deviations for Ethanol Activity σ (a_1) for the System Ethanol (1) + PEG400 (2) at Different Temperatures

T/K	χ_{12}	σ (a_1)
298.15	0.4751	0.0025
308.15	0.4093	0.0027
318.15	0.2664	0.0024
328.15	0.2271	0.0024

The deviations of the viscosities from the ideal mixture values can be calculated as[26]

$$\Delta\eta = \eta - \sum_{i=1}^{2} (x_i \eta_i) \tag{7}$$

where η_i is the dynamic viscosity of the pure component i. The experimental dynamic viscosity, η, viscosity deviations, $\Delta\eta$, and data for the ethanol + PEG system, as a function of PEG mole fraction, x_2, at T = (288.15 to 328.15) K are collected in Table 5. Grunberg and Nissan proposed an equation[27] connecting the viscosity and strength of interaction as follows

$$\ln \eta = x_1 \ln \eta_1 + (1 - x_1) \ln \eta_2 + x_1 x_2 \epsilon \tag{8}$$

where ϵ is the interaction parameter. The obtained values of ϵ for different temperatures are listed in Table 6. A plot of $\Delta\eta$ values versus polymer mole fraction is shown in Figure 4 for the ethanol + PEG system. As can be seen from Figure 4, viscosity deviations are negative over the entire composition range and over the five temperatures. However, as can be seen from Table 5 at T = (318.15 and 328.15) K and at the extremely polymer-rich region, the viscosity deviation values are slightly positive. Table 6 shows that the values of the interaction parameter, ϵ, are positive.

Correlation of Data. Ethanol activity values a_1 at each temperature reported in Table 1 were fitted to the original Flory–Huggins model[28] which has the following form

$$\ln a_1 = \ln z + \left(1 - \frac{1}{r_2}\right)(1 - z) + \chi_{12}(1 - z)^2 \tag{9}$$

In eq 9, z is the volume fraction of solvent; χ_{12} is the Flory parameter; and r_2 is the ratio of the molar volumes of polymer and solvent.

The result of fitting to eq 9 is given in Table 7. The standard deviations σ (a_1) given in Table 7 indicate that eq 9 represents the experimental ethanol activity data fairly well. The χ_{12} value reported in Table 7 decreases as the temperature increases. This decrease in χ_{12} indicates that as the temperature increases the interaction between PEG and ethanol becomes stronger. However, since there is little difference between the obtained χ_{12} values, the temperature has only a small effect on the interaction between PEG and ethanol.

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

$$\ln a_1 = \ln z + \left(1 - \frac{1}{r_2}\right)(1 - z) + \left[\frac{d_0}{1 - f(1 - z)} + \frac{d_1}{T[1 - f(1 - z)]} + \frac{d_2 \ln T}{1 - f(1 - z)}\right](1 - z)^2 \tag{10}$$

given by Bae et al.[29] was known to be successful in representing the concentration as well as temperature dependency of the

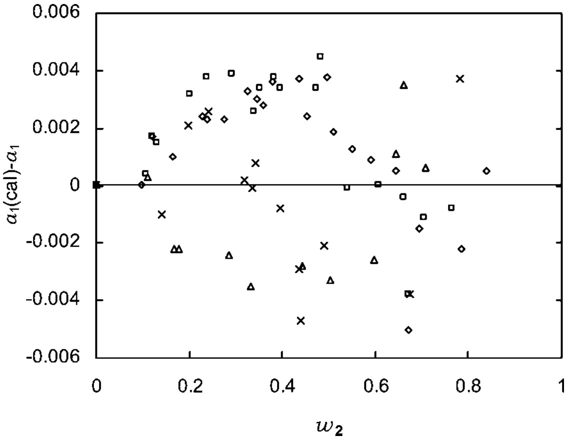

Figure 5. Difference between the experimental and calculated ethanol activities with the modified Flory–Huggins model (eq 10) at different temperatures: ◇, 298.15 K; □, 308.15 K; △, 318.15 K; ×, 328.15 K.

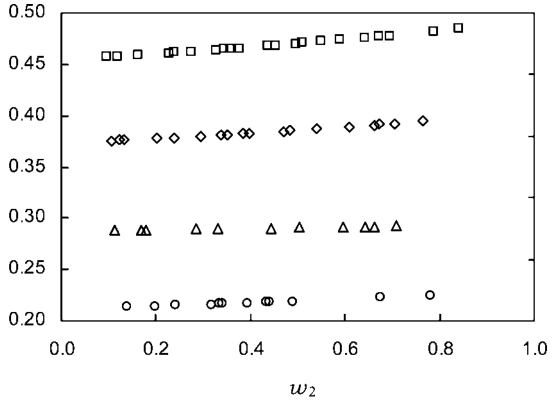

Figure 6. Variation of the Flory parameter χ_{12} with concentration and temperature for the ethanol (1) + PEG400 (2) system: □, 298.15 K; ◇, 308.15 K: △, 318.15 K: ○, 328.15 K.

solvent activity data in binary polymer + solvent systems. Therefore, we also fitted the experimental ethanol activity data of Table 1 to eq 10. The obtained parameters d_0, d_1, d_2, f, and standard deviation σ (a_1) are, respectively, 28.660, −637.667, −4.575, 0.079, and 0.0031. To see the performance of eq 10 in representing solvent activity data, the lines generated for ethanol activity at (298.15 and 328.15) K were obtained using the parameters of eq 10, and these are also shown in Figure 1. Differences between the experimental and calculated ethanol activities with the modified Flory–Huggins model (eq 10) are shown at different temperatures in Figure 5.

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

$$\chi_{12}(T, z) = \frac{d_0}{1 - f(1 - z)} + \frac{d_1}{T[1 - f(1 - z)]} + \frac{d_2 \ln T}{1 - f(1 - z)} \tag{11}$$

The variation of the Flory parameter χ_{12} with PEG mass fraction and the temperature were obtained from eq 11, and the corresponding plot is shown in Figure 6. Figure 6 shows that the modified Flory–Huggins model gives the χ_{12} values, which decrease by an increase in temperature, similar to the trend obtained by the original Flory–Huggins model as reported in Table 7. Also, as can be seen from Tables 6 and 7, the same trend is observed for interaction parameter ϵ and the Flory parameter χ_{12} at different temperatures.

Table 8. Parameters of Equation 12 with a Degree of Polynomial Expansion $N = 3$ or 4 for V^E along with the Corresponding Standard Deviations, σ (V^E), for the Ethanol (1) + PEG400 (2) System at Different Temperatures

T/K	B_0	B_1	B_2	B_3	B_4	σ (V^E)/(cm^3·mol^{-1})
288.15	−2.904	1.890	−2.748	2.810	–	0.018[a]
	−2.969	1.858	−1.795	2.888	−1.479	0.015[b]
298.15	−3.025	2.039	−3.009	2.945	–	0.019[a]
	−3.100	2.003	−1.893	3.037	−1.733	0.016[b]
308.15	−3.164	2.085	−3.229	3.229	–	0.019[a]
	−3.252	2.042	−1.932	3.335	−2.014	0.014[b]
318.15	−3.338	2.217	−3.455	3.495	–	0.020[a]
	−3.430	2.172	−2.087	3.607	−2.124	0.015[b]
328.15	−3.568	2.477	−3.674	3.521	–	0.021[a]
	−3.666	2.430	−2.226	3.640	−2.248	0.016[b]

[a] Degree of polynomial expansion, N, in eq 12 is 3. [b] Degree of polynomial expansion, N, in eq 12 is 4.

Table 9. Parameters of Equation 12 with a Degree of Polynomial Expansion $N = 3$ or 4 for $K^E{}_{s,m}$ along with the Corresponding Standard Deviations, σ ($K^E{}_{s,m}$), for the Ethanol (1) + PEG400 (2) System at Different Temperatures

T/K	B_0	B_1	B_2	B_3	B_4	$10^7\sigma$ ($K^E{}_{s,m}$) (cm^3·mol^{-1}·kPa^{-1})
288.15	−332.64	233.78	−470.85	158.50	–	4.8[a]
	−359.22	220.87	−79.18	190.60	−608.09	3.2[b]
298.15	−372.54	264.45	−535.17	210.61	–	5.3[a]
	−402.48	249.91	−94.03	246.77	−684.9	3.3[b]
308.15	−418.11	298.01	−608.41	266.14	–	5.9[a]
	−452.03	281.53	−108.61	307.10	−775.98	3.6[b]
318.15	−470.09	335.98	−693.52	331.13	–	6.6[a]
	−508.45	317.35	−128.30	377.46	−877.55	3.9[b]
328.15	−528.66	381.38	−788.27	409.12	–	7.2[a]
	−571.88	360.38	−151.34	461.32	−988.89	4.1[b]

[a] Degree of polynomial expansion, N, in eq 12 is 3. [b] Degree of polynomial expansion, N, in eq 12 is 4.

Table 10. Parameters of Equation 12 for $\Delta\eta$ along with the Corresponding Standard Deviations, σ ($\Delta\eta$), for the Ethanol (1) + PEG400 (2) System at Different Temperatures

T/K	B_0	B_1	B_2	B_3	$\sigma(\Delta\eta)$/(mPa·s)
288.15	−75.209	54.019	12.457	5.041	0.48
298.15	−29.909	29.371	−5.297	−8.106	0.16
308.15	−11.160	18.407	−4.110	−6.070	0.11
318.15	−3.381	10.137	−0.460	−5.407	0.12
328.15	−0.391	6.372	−1.263	−1.634	0.12

All the calculated deviations were correlated by means of the Redlich–Kister equation[30]

$$Q = x_2(1 - x_2)\sum_{p=0}^{N} B_p(2x_2 - 1)^p \tag{12}$$

where Q stands for V^E, $K^E{}_{s,m}$, and $\Delta\eta$; B_p represents the fitting coefficients; and N is the degree of the polynomial expansion. The standard deviations, σ, between the calculated, Q_{calcd}, and the experimental, Q_{exptl}, values have been estimated by using

$$\sigma = \left(\frac{\sum_{i=1}^{n_{\text{DAT}}} (Q_{\text{exptl}} - Q_{\text{calcd}})^2}{n_{\text{DAT}}}\right)^{1/2} \tag{13}$$

where n_{DAT} is the number of experimental points. The obtained adjustable parameters, B_p, are summarized in Tables 8, 9, and 10, together with the standard deviations, σ. Using eq 12 with $N = 4$ for V^E and $K^E{}_{s,m}$ and $N = 3$ for $\Delta\eta$ and the corresponding parameters reported in Tables 8, 9, and 10, the lines generated for V^E, $K^E{}_{s,m}$, and $\Delta\eta$ were obtained,

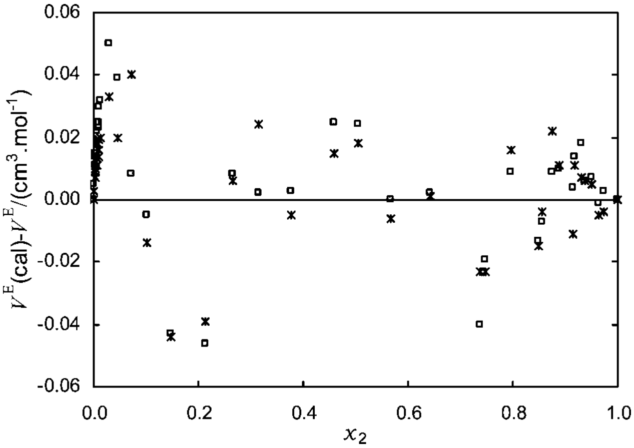

Figure 7. Difference between the experimental and calculated excess molar volumes, V^E, with the Redlich–Kister equation (eq 12) at two temperatures: *, 288.15 K; □, 328.15 K.

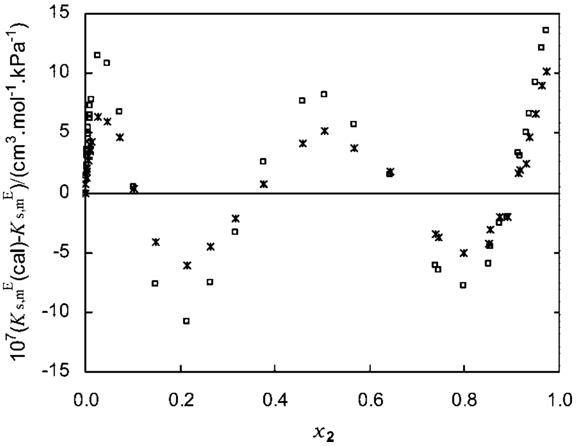

Figure 8. Difference between the experimental and calculated excess molar isentropic compression, $K^E_{s,m}$, with the Redlich–Kister equation (eq 12) at two temperatures: *, 288.15 K; □, 328.15 K.

and these were also, respectively, shown in Figures 2, 3, and 4 for the five studied isotherms. Slightly higher standard deviations for V^E and $K^E_{s,m}$ are obtained when we use eq 12 with $N = 3$, as can be seen in Tables 8 and 9. Differences between the experimental and calculated excess molar volumes, excess molar isentropic compressions, and viscosity deviation with the Redlich–Kister equation (eq 12) are shown, respectively, in Figures 7, 8, and 9 at two temperatures [(288.15 and 328.15) K] as examples.

Conclusions

Ethanol activity data were determined for the ethanol + 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 ethanol activity and the Flory parameter decrease as the temperature is increased. From measurements of density, speed of sound, and viscosity at $T = (288.15$ to $328.15)$ K, the values for excess molar volume, excess molar isentropic compression, and viscosity deviation for ethanol + PEG400 were calculated. In the entire composition range and at all working temperatures, excess molar volume, excess molar isentropic compression, and viscosity deviation are negative. The behavior of these magnitudes seems to suggest that increasing temperature leads to an increase of the interactions between the system components (polymer and ethanol) and that the system is less compressible than the hypothetical ideal mixture.

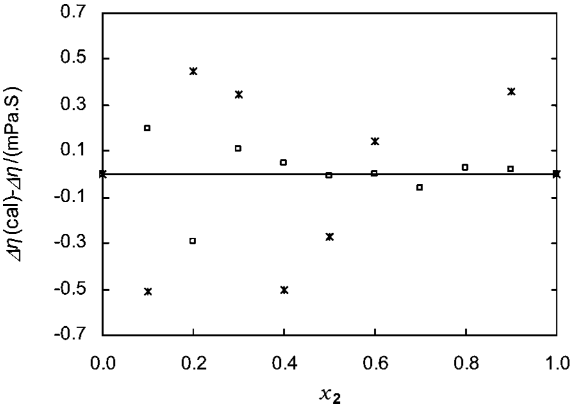

Figure 9. Difference between the experimental and calculated viscosity deviation $\Delta\eta$, with the Redlich–Kister equation (eq 12) at two temperatures: *, 288.15 K; □, 328.15 K.

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