Pressure, Volume, and Temperature for Mixtures of Poly(ethylene glycol methyl ether)-350 + Anisole and Poly(ethylene glycol)-200 + Anisole from 298 K to 338 K and Pressures up to 50 MPa

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PVT properties were measured for mixtures of poly(ethylene glycol methyl ether)-350 + anisole and poly(ethylene glycol)-200 + anisole at temperatures from 298 K to 338 K and pressures up to 50 MPa. Excess volumes are positive for these two polymer solution systems. The isothermal compressibilities were calculated with the aid of the Tait equation, which represented accurately the pressure effect on the liquid densities over the entire pressure range. The experimental specific volumes were correlated with the Flory−Orwoll−Vrij and the Schotte equations of state.

Introduction

Volumetric properties of polymeric materials and polymer solutions are needed in polymer processing. Phase equilibrium properties of polymer solutions, such as critical points and binodals, often depend strongly on pressure, temperature, and composition. Reliable *PVT* data of polymer solutions are fundamentally important to development of polymer equations of state that are applicable over a wide range of densities. Dee et al.[1] reported the characteristic parameters of the Flory−Orwoll−Vrij (FOV) equation of state for various polymer liquids, including polyethylene, poly(dimethyl siloxane), poly(ethylene glycol) (PEG), and poly(propylene glycol) (PPG). These parameters have been determined from *PVT* data in a temperature range from room temperature to 250 °C and at pressures up to 200 MPa. The densities (or specific volumes) of aqueous PEGs and of oligomeric propylene glycols were measured by Muller and Rasmussen[2] and also by Sandell and Goring[3] at atmospheric pressure. Earlier *PVT* data of polymers have been extensively compiled by Zoller and Walsh[4] over wide ranges of temperature and pressure. *PVT* data for associated polymer solutions have been reported recently, such as for poly(4-hydroxystyrene) + acetone (Compostizo et al.[5]), poly(4-hydroxystyrene) + tetrahydrofuran and + ethanol (Compostizo et al.[6]), and poly(propylene glycol) + *n*-hexane and + ethanol (Colin et al.[7]). These data were used to examine polymer equations of state for describing the hydrogen-bonding effects on the volumetric properties of polymer solutions. More recently, our research laboratory has made a series of *PVT* measurements for polymeric systems over a temperature range from 298.15 K to 338.15 K and at pressures up to 30 MPa: Lee et al.[8] determined the volumetric properties for poly(ethylene glycol methyl ether)-350 (PEGME-350), PEG-200, PEG-600, and the blended mixtures of PEGME-350 with either PEG-200 or PEG-600, Chang et al.[9] determined those for 10 fractionation cuts of PEG and PPG, and Lee et al.[10] determined those for polymer solutions of PEG-200 + 1-octanol and PEG-600 + 1-octanol. As a part of a continuation of these studies, the results of *PVT* measurements are reported in this work for PEGME-350 + anisole and PEG-200 + anisole at temperatures from 298 K to 338 K and pressures up to 50 MPa. These two polymer solution systems contain a common polar solvent and an associating oligomeric compound with different end-groups. The new experimental results complement information on volumetric behavior for the associated polymer solutions in response to the effects of temperature, pressure, and composition.

Experimental Section

Anisole (purity 99+ mass %) and the fractionation cuts of PEGME-350 and PEG-200 were purchased from Aldrich Chemical Co. (Milwaukee, WI). The number-average molecular weights (M_n) and the polydispersities (M_w/M_n) are approximately 358 and 1.099 for PEGME-350 and 210 and 1.112 for PEG-200, respectively. These values were determined with a matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) instrument. Each substance has been degassed by heat accompanied by agitation before use. The schematic diagram of the *PVT* apparatus is shown in Figure 1, which is similar to that of Chang and Lee.[11] The liquid mixture sample was prepared from the degassed compounds by mass to an accuracy of ±0.0001 in mass fraction and stored in the sample vessel (1). The sample was then delivered into a high-pressure densitometer (DMA 512 P, Anton Paar, 2) via a hand pump (model-2426-801, Ruska, 3). Pressure in the measuring cell was manipulated by the hand pump and monitored by a pressure transducer (model-PDCR 911, 0-70 MPa, Druck, 4) with a digital indicator (model-DPI 261, Druck, 5). Pressure measurements were accurate to ±0.1% at pressures higher than atmospheric. A thermostatic bath (6) with circulating water maintained the temperature of the measuring cell to within ±0.03 K. The cell and the circulation lines were well insulated. A precision digital thermometer (model-1506, Hart Scientific, 7) incorporated with a thermistor probe measured the bath temperature to an accuracy of ±0.02 K. The oscillation period (t_i) of sample *i* in the vibrating U tube was displayed by a DMA 60 processing

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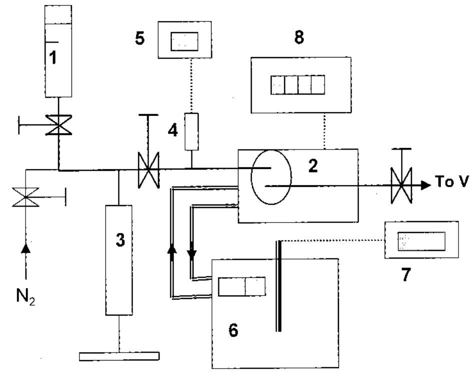

Figure 1. Schematic diagram of the *PVT* apparatus: (1) sample vessel; (2) DMA 512 P densitometer; (3) hand pump; (4) pressure transducer; (5) pressure indicator; (6) thermostatic bath; (7) thermometer; (8) DMA 60 processing unit.

unit (Anton Paar, 8) and was converted into density (ρ_i) via

$$\rho_i = A(t_i^2 - B) \tag{1}$$

where *A* and *B* are apparatus parameters determined by using the literature *PVT* data of two calibration fluids: pure water[12] and dry nitrogen.[13] The calibration was made at each temperature of interest over the pressure range (0.1−50) MPa. Parameter *A* decreases linearly with increase in both pressure and temperature. The calibration reproduced water densities with an average absolute deviation of 0.01% over the entire calibrated conditions. Ashcroft et al.[14] pointed out that viscosity changes between the samples and the calibration fluid could affect the accuracy of the density measurement by an oscillating densitometer. However, the viscosity effect is far below 0.1% on the density measurements. The accuracy of the densities reported in this work is estimated to within ±0.1%.

Results and Discussion

Table 1 lists the experimental densities (ρ) and the calculated isothermal compressibilities (κ_T) of anisole, PEGME-350, and PEG-200. The density of anisole is 0.9888 g·cm^{-3} at 298.15 K and 0.1 MPa, which is in good agreement with the literature value (0.9893 g·cm^{-3}) reported by Joshi et al.[15] Tables 2 and 3 present the results of the experimental ρ and calculated κ_T for PEGME-350 + anisole and PEG-200 + anisole, respectively. The isothermal densities at a given composition were correlated with the Tait equation:

$$\frac{\rho - \rho_0}{\rho} = C \ln\left(\frac{D + P}{D + 0.1}\right) \tag{2}$$

where ρ_0 is the density at 0.1 MPa. The optimized values of *C* and *D* were obtained by fitting the Tait equation to the density data with the following objective function (π):

$$\pi = [\sum_{k=1}^{n} |\rho_{k,\mathrm{calc}} - \rho_{k,\mathrm{exp}}|/\rho_{k,\mathrm{exp}})]/n \tag{3}$$

where *n* is the number of data points. $\rho_{k,\mathrm{calc}}$ and $\rho_{k,\mathrm{exp}}$ refer to the calculated and the experimental densities for the *k*th point, respectively. Table 4 reports the calculated results including the values of *C*, *D*, and π. The Tait equation correlates accurately the isothermal densities over the entire pressure range. The tabulated isothermal compressibility was calculated with the following equation:

Table 1. Experimental Density and Calculated Isothermal Compressibility for Anisole, PEGME-350, and PEG-200

	T/K = 298.15		T/K = 318.15		T/K = 338.15	
P/MPa	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}
			Anisole			
0.1	0.9888	7.06	0.9689	7.42	0.9564	9.76
10	0.9951	6.43	0.9767	6.93	0.9581	8.58
20	1.0012	5.91	0.9836	6.65	0.9655	7.65
30	1.0068	5.47	0.9898	6.12	0.9724	6.91
40	1.0122	5.09	0.9954	5.78	0.9789	6.31
50	1.0172	4.77	1.0010	5.49	0.9851	5.80
			PEGME-350			
0.1	1.0827	5.57	1.0668	5.25	1.0491	6.50
10	1.0888	5.00	1.0721	4.97	1.0559	5.87
20	1.0934	4.20	1.0774	4.72	1.0613	5.35
30	1.0984	3.86	1.0825	4.49	1.0664	4.92
40	1.1025	3.85	1.0872	4.29	1.0721	4.55
50	1.1071	3.61	1.0917	4.11	1.0767	4.24
			PEG-200			
0.1	1.1179	4.89	1.1008	4.93	1.0903	5.14
10	1.1235	4.42	1.1088	4.67	1.0930	4.82
20	1.1278	4.02	1.1131	4.17	1.0970	4.46
30	1.1316	3.69	1.1176	3.92	1.1019	4.02
40	1.1361	3.42	1.1215	3.65	1.1064	3.81
50	1.1401	3.18	1.1256	3.43	1.1120	3.25

$$\kappa_T = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,x} = \frac{V_0}{V}\left(\frac{C}{D + P}\right) \tag{4}$$

where *V* is the molar volume, V_0 is the molar volume at 0.1 MPa, and the constants *C* and *D* are parameters of the Tait equation.

The volume change of mixing or excess volume (V^E) is related to the molecular interactions in a mixture. The excess volume can be calculated from experimental density data. The uncertainty of the calculated excess volumes was estimated to be about ±0.05 cm^3·mol^{-1}. Positive excess volumes were exhibited from these two polymer solution systems, implying that volume expansion occurs upon blending anisole with these oligomeric substances. Figure 2 shows the effects of both temperature and pressure on V^E for PEG-200 + anisole. The excess volumes appear to increase with an increase of temperature and with a decrease of pressure. Similar behavior is also found in PEGME-350 + anisole. The excess volumes at constant temperature and pressure were correlated with a Redlich−Kister type equation:

$$V^E/x_1x_2 = \sum_{k=1}^{3} E_k(x_1 - x_2)^{k-1} \tag{5}$$

The optimized values of E_k as determined by a least-squares algorithm are tabulated in Table 5, and the calculated results are represented by the dashed curves in Figure 2.

PVT Data Correlation with Equations of State

The *PVT* data of polymers are useful for development of correlation methods. The experimental specific volumes

Table 2. Experimental Density and Calculated Isothermal Compressibility for PEGME-350 (1) + Anisole (2)

	T/K = 298.15		T/K = 318.15		T/K = 338.15	
P/ MPa	ρ/ g·cm^{-3}	$10^4\kappa_T$/ MPa^{-1}	ρ/ g·cm^{-3}	$10^4\kappa_T$/ MPa^{-1}	ρ/ g·cm^{-3}	$10^4\kappa_T$/ MPa^{-1}
$w_1 = 0.2689$[a] ($x_1 = 0.100$)[b]						
0.1	1.0119	6.06	0.9941	6.33	0.9743	7.84
10	1.0177	5.71	1.0004	6.08	0.9819	7.24
20	1.0234	5.38	1.0060	5.85	0.9881	6.71
30	1.0290	5.10	1.0121	5.63	0.9946	6.26
40	1.0339	4.85	1.0176	5.44	1.0012	5.87
50	1.0389	4.62	1.0229	5.25	1.0066	5.53
$w_1 = 0.4528$ ($x_1 = 0.200$)						
0.1	1.0289	5.86	1.0111	6.25	0.9926	6.88
10	1.0345	5.46	1.0171	5.92	0.9992	6.59
20	1.0400	5.11	1.0232	5.62	1.0057	6.32
30	1.0453	4.80	1.0287	5.34	1.0118	6.06
40	1.0502	4.53	1.0339	5.10	1.0181	5.84
50	1.0551	4.85	1.0393	4.88	1.0238	5.62
$w_1 = 0.5866$ ($x_1 = 0.300$)						
0.1	1.0421	5.89	1.0243	6.39	1.0057	6.83
10	1.0479	5.37	1.0305	5.88	1.0131	6.55
20	1.0532	4.93	1.0363	5.45	1.0192	6.27
30	1.0580	4.56	1.0418	5.08	1.0252	6.02
40	1.0630	4.25	1.0470	4.76	1.0312	5.79
50	1.0678	3.98	1.0520	4.48	1.0360	5.58
$w_1 = 0.6882$ ($x_1 = 0.400$)						
0.1	1.0509	5.48	1.0337	5.70	1.0147	7.72
10	1.0565	5.18	1.0395	5.46	1.0227	6.61
20	1.0618	4.91	1.0450	5.24	1.0279	5.98
30	1.0668	4.66	1.0503	5.03	1.0339	5.37
40	1.0715	4.44	1.0553	4.84	1.0398	4.89
50	1.0766	4.24	1.0608	4.67	1.0445	4.48
$w_1 = 0.7680$ ($x_1 = 0.500$)						
0.1	1.0572	5.50	1.0399	5.94	1.0223	6.19
10	1.0627	5.08	1.0457	5.47	1.0288	5.94
20	1.0678	4.78	1.0510	5.07	1.0341	5.69
30	1.0727	4.40	1.0564	4.72	1.0401	5.46
40	1.0774	4.12	1.0613	4.42	1.0458	5.26
50	1.0820	3.88	1.0662	4.16	1.0512	5.07
$w_1 = 0.8324$ ($x_1 = 0.600$)						
0.1	1.0644	5.04	1.0468	5.83	1.0294	6.07
10	1.0694	4.72	1.0526	5.36	1.0357	5.77
20	1.0745	4.60	1.0577	4.96	1.0409	5.49
30	1.0793	4.32	1.0630	4.62	1.0467	5.23
40	1.0839	4.13	1.0679	4.32	1.0525	5.01
50	1.0884	3.95	1.0728	4.10	1.0574	4.80
$w_1 = 0.8854$ ($x_1 = 0.700$)						
0.1	1.0691	5.33	1.0521	5.46	1.0344	5.93
10	1.0748	5.10	1.0577	5.20	1.0409	5.74
20	1.0797	4.54	1.0632	4.96	1.0462	5.55
30	1.0843	4.33	1.0679	4.75	1.0520	5.38
40	1.0890	4.08	1.0732	4.55	1.0576	5.22
50	1.0935	3.86	1.0780	4.37	1.0625	5.06
$w_1 = 0.9298$ ($x_1 = 0.800$)						
0.1	1.0727	5.64	1.0549	6.20	1.0391	5.87
10	1.0784	5.03	1.0612	5.60	1.0447	5.49
20	1.0830	4.53	1.0669	5.13	1.0501	5.15
30	1.0882	4.12	1.0721	4.72	1.0557	4.85
40	1.0923	3.78	1.0767	4.37	1.0614	4.58
50	1.0971	3.50	1.0815	4.08	1.0655	4.35
$w_1 = 0.9675$ ($x_1 = 0.900$)						
0.1	1.0772	5.62	1.0606	6.10	1.0442	5.37
10	1.0832	5.01	1.0668	5.45	1.0497	5.22
20	1.0881	4.58	1.0721	4.91	1.0549	5.07
30	1.0929	4.10	1.0772	4.48	1.0601	4.93
40	1.0968	3.87	1.0819	4.12	1.0660	4.80
50	1.1016	3.13	1.0862	3.81	1.0706	4.68

[a] w_1: mass fraction of component 1. [b] x_1: mole fraction of component 1; calculated with the molecular weights of 358 and 108.140 for PEGME-350 and anisole, respectively.

Table 3. Experimental Density and Calculated Isothermal Compressibility for PEG-200 (1) + Anisole (2)

	T/K = 298.15		T/K = 318.15		T/K = 338.15	
P/ MPa	ρ/ g·cm^{-3}	$10^4\kappa_T$/ MPa^{-1}	ρ/ g·cm^{-3}	$10^4\kappa_T$/ MPa^{-1}	ρ/g·cm^{-3}	$10^4\kappa_T$/ MPa^{-1}
$w_1 = 0.1775$[a] ($x_1 = 0.100$)[b]						
0.1	1.0061	6.15	0.9879	6.70	0.9692	8.52
10	1.0122	5.83	0.9943	6.37	0.9774	7.93
20	1.0177	5.55	1.0006	6.07	0.9832	7.22
30	1.0235	5.29	1.0065	5.80	0.9889	6.43
40	1.0287	5.06	1.0122	5.56	0.9961	5.91
50	1.0336	4.84	1.0176	5.33	1.0020	5.67
$w_1 = 0.3268$ ($x_1 = 0.200$)						
0.1	1.0241	6.04	1.0061	6.54	0.9867	7.76
10	1.0298	5.57	1.0123	6.10	0.9945	7.12
20	1.0357	5.18	1.0185	5.71	1.0005	6.56
30	1.0406	4.83	1.0242	5.37	1.0068	6.09
40	1.0456	4.53	1.0293	5.07	1.0131	5.70
50	1.0504	4.27	1.0345	4.78	1.0187	5.35
$w_1 = 0.4542$ ($x_1 = 0.300$)						
0.1	1.0405	5.47	1.0245	5.84	1.0062	5.91
10	1.0462	5.17	1.0306	5.31	1.0125	5.71
20	1.0512	4.90	1.0346	4.87	1.0169	5.52
30	1.0561	4.65	1.0397	4.51	1.0230	5.34
40	1.0611	4.44	1.0448	4.19	1.0290	5.18
50	1.0658	4.24	1.0499	3.93	1.0339	5.03
$w_1 = 0.5642$ ($x_1 = 0.400$)						
0.1	1.0541	5.19	1.0367	6.21	1.0184	6.92
10	1.0596	4.96	1.0431	5.68	1.0258	6.37
20	1.0644	4.74	1.0485	5.22	1.0310	5.89
30	1.0697	4.54	1.0536	4.84	1.0369	5.48
40	1.0740	4.36	1.0585	4.51	1.0428	5.13
50	1.0789	4.20	1.0634	4.23	1.0481	4.82
$w_1 = 0.6600$ ($x_1 = 0.500$)						
0.1	1.0665	5.40	1.0484	7.05	1.0327	5.42
10	1.0724	5.01	1.0554	5.91	1.0385	5.31
20	1.0770	4.66	1.0605	5.09	1.0434	5.20
30	1.0821	4.36	1.0657	4.48	1.0488	5.18
40	1.0863	4.10	1.0705	3.99	1.0544	5.00
50	1.0910	3.87	1.0750	3.61	1.0596	4.91
$w_1 = 0.7444$ ($x_1 = 0.600$)						
0.1	1.0773	5.29	1.0611	5.00	1.0444	5.00
10	1.0832	4.92	1.0663	4.80	1.0502	4.96
20	1.0880	4.59	1.0713	4.62	1.0543	4.92
30	1.0926	4.31	1.0760	4.45	1.0594	4.88
40	1.0969	4.06	1.0805	4.29	1.0651	4.84
50	1.1017	3.84	1.0859	4.15	1.0705	4.80
$w_1 = 0.8192$ ($x_1 = 0.700$)						
0.1	1.0900	5.18	1.0728	5.51	1.0566	5.14
10	1.0933	4.81	1.0783	4.92	1.0619	4.92
20	1.0985	4.32	1.0835	4.45	1.0668	4.71
30	1.1033	4.04	1.0880	4.05	1.0716	4.52
40	1.1073	3.72	1.0925	3.73	1.0770	4.35
50	1.1117	3.61	1.0958	3.45	1.0813	4.19
$w_1 = 0.8859$ ($x_1 = 0.800$)						
0.1	1.1008	4.38	1.0844	4.77	1.0659	7.66
10	1.1054	4.19	1.0894	4.50	1.0737	6.08
20	1.1101	4.01	1.0941	4.24	1.0779	5.02
30	1.1143	3.85	1.0988	4.04	1.0834	4.29
40	1.1186	3.71	1.1031	3.84	1.0884	3.74
50	1.1227	3.56	1.1075	3.67	1.0934	3.33
$w_1 = 0.9459$ ($x_1 = 0.900$)						
0.1	1.1062	4.18	1.0900	4.32	1.0780	4.82
10	1.1108	4.01	1.0943	4.24	1.0834	4.32
20	1.1149	3.86	1.0989	4.17	1.0870	3.91
30	1.1195	3.72	1.1038	4.12	1.0917	3.57
40	1.1234	3.58	1.1083	4.03	1.0946	3.28
50	1.1272	3.46	1.1135	3.97	1.0986	3.04

[a] w_1: mass fraction of component 1. [b] x_1: mole fraction of component 1; calculated with the molecular weights of 210 and 108.140 for PEG-200 and anisole, respectively.

Table 4. Results of Density Correlation with the Tait Equation

	PEGME-350 (1) + Anisole (2)			PEG-200 (1) + Anisole (2)		
x_1	C	D/MPa	$10^2\pi^a$	C	D/MPa	$10^2\pi^a$
T/K = 298.15						
0.0	0.07528	109.6	0.000	0.07528	109.6	0.000
0.100	0.08692	143.4	0.000	0.10078	163.8	0.002
0.200	0.07248	123.5	0.001	0.06705	111.0	0.000
0.300	0.05655	95.9	0.001	0.08452	154.4	0.000
0.400	0.08427	153.6	0.002	0.09743	187.6	0.000
0.500	0.06086	110.5	0.001	0.06269	115.8	0.001
0.600	0.08173	162.0	0.002	0.06478	122.4	0.000
0.700	0.06440	120.8	0.000	0.07216	107.5	0.001
0.800	0.04346	77.0	0.001	0.08544	194.8	0.001
0.900	0.04692	83.4	0.001	0.09068	217.0	0.000
1.000	0.04814	86.4	0.000	0.04299	87.8	0.000
T/K = 318.15						
0.0	0.01325	193.4	0.004	0.01325	193.4	0.004
0.100	0.01313	207.5	0.000	0.01139	170.0	0.000
0.200	0.09792	156.5	0.002	0.08140	124.3	0.000
0.300	0.06844	107.0	0.000	0.05580	95.7	0.002
0.400	0.11189	196.1	0.001	0.06120	98.5	0.001
0.500	0.06361	106.9	0.002	0.03503	49.6	0.000
0.600	0.06187	106.0	0.001	0.01067	213.1	0.001
0.700	0.09798	179.5	0.002	0.04358	79.0	0.001
0.800	0.05552	89.4	0.000	0.07216	151.1	0.000
0.900	0.04763	77.9	0.000	0.01940	449.9	0.001
1.000	0.08532	162.5	0.000	0.06223	104.9	0.002
T/K = 338.15						
0.0	0.06722	68.9	0.003	0.06722	68.9	0.003
0.100	0.08357	106.5	0.000	0.05691	89.2	0.003
0.200	0.12935	187.8	0.000	0.07765	100.0	0.002
0.300	0.12918	188.9	0.000	0.01419	240.1	0.003
0.400	0.04974	64.3	0.001	0.07236	104.4	0.000
0.500	0.11936	192.6	0.001	0.20650	381.2	0.003
0.600	0.10036	165.2	0.000	0.3711	742.0	0.002
0.700	0.14548	245.3	0.001	0.1006	195.8	0.003
0.800	0.07546	128.4	0.001	0.0281	36.5	0.001
0.900	0.14921	277.6	0.000	0.0389	80.6	0.000
1.000	0.05648	86.8	0.003	0.04179	86.5	0.001

[a] π: defined as in eq 3.

were correlated with two polymer equations of state (EOS): the Flory−Orwoll−Vrij (FOV)[16] and the Schotte.[17] These EOS were expressed as follows.

The FOV EOS:

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{\bar{V}^{1/3}}{\bar{V}^{1/3} - 1} - \frac{1}{\bar{T}\bar{V}} \tag{6}$$

The Schotte EOS:

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{RT^*}{P^*MV^*}\left(1 - \frac{1}{\bar{V}^{1/3}}\right) + \frac{1}{\bar{V}^{1/3} - 1} - \frac{2}{\bar{T}\bar{V}} \tag{7}$$

where M is the molecular weight, $\bar{P} = P/P^*$, $\bar{V} = V/V^*$, and $\bar{T} = T/T^*$. The model parameters P^*, V^*, and T^* are characteristic pressure, specific volume, and temperature, respectively, which were determined by fitting the EOS to experimental PVT data. Table 6 lists the calculated results for anisole, PEGME-350, and PEG-200, where the characteristic parameters of PEGME-350 and PEG-200 are taken from Lee et al.[8] These tabulated characteristic parameters were further employed to calculate the specific volumes of the polymer solutions via the following mixing rules:[17]

$$V_m^* = \left[M_m\left(\frac{\Psi_1}{M_1V_1^*} + \frac{\Psi_2}{M_2V_2^*}\right)\right]^{-1} \tag{8}$$

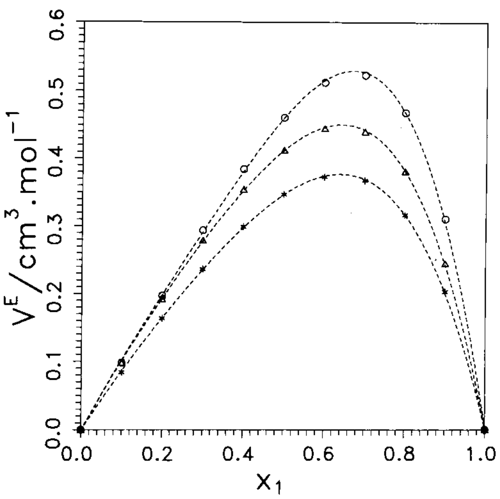

Figure 2. Variations of excess volume with composition for PEG-200 (1) + anisole (2) at 338.15 K and 0.1 MPa (○); 338.15 K and 50 MPa (△); 298.15 K and 50 MPa (*); Redlich−Kister equation (- - -).

Table 5. Results of Excess Volume Correlation with the Redlich−Kister Equation

	PEGME-350 (1) + Anisole (2)			PEG-200 (1) + Anisole (2)			
P/MPa	E_1	E_2	10^2(AAD)[a]	E_1	E_2	E_3	10^2(AAD)[a]
T/K = 298.15							
0.1	2.173	−0.251	1.9	1.875	0.125	0.954	1.8
10.0	2.192	−0.312	2.1	1.865	0.136	0.912	1.9
20.0	2.234	−0.348	2.1	1.912	0.147	0.898	1.7
30.0	2.266	−0.365	2.0	2.034	0.154	0.862	1.8
40.0	2.315	−0.381	2.1	2.054	0.162	0.855	1.9
50.0	2.337	−0.394	2.1	2.065	0.182	0.843	2.0
T/K = 318.15							
0.1	2.263	−0.241	1.9	1.754	0.141	0.754	1.8
10.0	2.297	−0.234	1.9	1.789	0.152	0.753	1.9
20.0	2.354	−0.224	2.0	1.823	0.164	0.741	2.1
30.0	2.392	−0.218	2.1	1.846	0.175	0.733	1.7
40.0	2.424	−0.205	2.0	1.886	0.182	0.722	1.9
50.0	2.496	−0.197	2.1	1.894	0.194	0.715	2.1
T/K = 338.15							
0.1	2.318	−0.165	1.9	1.865	0.143	0.641	2.1
10.0	2.325	−0.216	1.8	1.897	0.152	0.632	2.2
20.0	2.335	−0.235	1.9	1.914	0.161	0.611	2.0
30.0	2.412	−0.257	2.1	1.924	0.173	0.587	1.9
40.0	2.465	−0.259	2.1	1.945	0.184	0.542	1.9
50.0	2.494	−0.261	2.0	1.964	0.192	0.514	2.1

[a] AAD/(cm^3·mol^{-1}) = $(1/n)\sum_{i=1}^{n}|V^E{}_{i,\mathrm{calc}} - V^E{}_{i,\mathrm{exp}}|$, where n is the number of data points.

$$T_m^* = \frac{P_m^*}{\dfrac{\Psi_1P_1^*}{T_1^*} + \dfrac{\Psi_2P_2^*}{T_2^*}} \tag{9}$$

and

$$P_m^* = \Psi_1^2P_1^* + \Psi_2^2P_2^* + 2\Psi_1\Psi_2P_{12}^* \tag{10}$$

with

$$\Psi_i = \frac{w_iV_i^*}{w_1V_1^* + w_2V_2^*} \tag{11}$$

and

Table 6. Results of Specific Volume Correlation with the Equations of State for "Pure" Compounds

	FOV EOS				Schotte EOS			
compound	P^*/MPa	T^*/K	V^*/cm^3·g^{-1}	AAD^a/cm^3·g^{-1}	P^*/MPa	T^*/K	V^*/cm^3·g^{-1}	AAD^a/cm^3·g^{-1}
anisole	643.0	5379	0.8173	0.000 29	652.8	4736	0.8052	0.000 32
PEGME-350^b	707.2	6122	0.7705	0.000 25	722.9	5395	0.7591	0.000 19
PEG-200^b	738.2	6541	0.7566	0.000 17	783.3	5728	0.7444	0.000 12

^{a} AAD $= (1/n)\sum_{k=1}^{n}|V_{k,\mathrm{calc}} - V_{k,\mathrm{exp}}|$. ^{b} Parameters P^*, T^*, and V^* were taken from Lee et al.[8]

Table 7. Results of Specific Volume Correlation with the Equations of State for Polymer Solutions

	FOV EOS		Schotte EOS	
mixture (1) + (2)	Δ_{12}	AAD%^{a}	Δ_{12}	AAD%^{a}
PEGME-350 + anisole	−0.1294	0.22	−0.1290	0.21
PEG-200 + anisole	−0.0299	0.15	−0.0317	0.14

^{a} AAD% $= (100/n)\sum_{k=1}^{n}|V_{k,\mathrm{calc}} - V_{k,\mathrm{exp}}|/V_{k,\mathrm{exp}}$.

$$P_{12}^* = (1 - \Delta_{12})(P_1^* P_2^*)^{0.5} \tag{12}$$

where Ψ_i, M_i, and w_i stand for the segment volume fraction, the number average molecular weight, and the weight fraction of component i, respectively. Δ_{12} in eq 12 is a binary interaction constant that was determined from the *PVT* data for each binary system. The calculated results are reported in Table 7. Both the FOV and the Schotte EOS represent quantitatively the *PVT* behavior of PEGME-350 + anisole and PEG-200 + anisole over the entire experimental conditions.

Conclusions

PVT data have been measured for PEGME-350 + anisole and PEG-200 + anisole at temperatures from 298 K to 338 K and pressures up to 50 MPa. Volume expansion (positive excess volume) was found upon mixing anisole with either PEGME-350 or PEG-200. The pressure effect on the isothermal densities was represented accurately by the Tait equation, which was then used to calculate isothermal compressibilities. Both the FOV and the Schotte EOS correlated well the *PVT* data of the polymer solutions.

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