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Pressure–volume–temperature properties for binary and ternary polymer solutions of poly(ethylene glycol), poly(propylene glycol), and poly(ethylene glycol methyl ether) with anisole

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Abstract

Pressure–volume–temperature properties were measured for polymer solutions of poly(propylene glycol) (PPG) + anisole, polymer blends of PPG + poly(ethylene glycol methyl ether) (PEGME), and the blends of PPG + PEGME and poly(ethylene glycol) (PEG) + PPG with anisole at temperatures from 298.15 to 348.15 K and pressures up to 50 MPa. The Tait equation represents accurately the pressure effect on the liquid densities over the entire pressure range. The excess volumes change from positive to negative as increasing the mole fraction of PPG in the binary systems of PPG + anisole and PPG + PEGME. The volumetric data of the related binary systems were correlated with the Flory–Orwoll–Vrij and the Schotte equations of state to determine the binary parameters. By using these determined binary parameters, both equations predicted the specific volumes of the polymer blends with anisole to average absolute deviations of better than 0.13%.

Keywords: PVT properties; Polymer solutions; Polymer blends

1. Introduction

Pressure–volume–temperature ($P-V-T$) properties of polymer solutions are useful for understanding the intermolecular interactions and for engineering applications. These data form a basis for determination of model parameters, which is essential to calculate the thermodynamic properties for the polymeric mixtures. Zoller and Walsh [1] made an elaborative $P-V-T$ data collection for a wide variety of 'pure' polymeric materials and a few for polymer blends. The $P-V-T$ data of polymer solutions and polymer blends are relatively limited, especially for multicomponent systems. Muller and Rasmussen [2] and Sandell and Goring [3] reported the specific volumes of aqueous PEGs and of oligomeric propylene glycols. The data for associated polymer solutions and polymer blends have been reported in recent years, including poly(4-hydroxystyrene) + acetone [4], poly(4-hydroxystyrene) + tetrahydrofuran + ethanol [5], PPG + *n*-hexane + ethanol [6] and PEG + PPG [7]. Panayiotou and Sanchez [8] used those data to examine the lattice-fluid equations of state for describing the hydrogen-bonding effects on the volumetric properties of polymer solutions. Our research group has also made a series of $P-V-T$ measurements for various polymer solutions and polymer blends, containing PEG, PPG, and PEGME: Lee et al. [9] reported the volumetric properties for PEGME-350, PEG-200, PEG-600, and the blended mixtures of PEGME-350 with either PEG-200 or PEG-600, Chang et al. [10] for ten fractionation cuts of PEG and PPG, Lee et al. [11] for polymer solutions of PEG-200 + 1-octanol and PEG-600 + 1-octanol, Lee et al. [12] for PEGME-350 + anisole and PEG-200 + anisole, and Lin et al. [13] for the binary polymer solutions of PPG-4000 with 1-octanol and acetophenone. In the present study, the $P-V-T$ properties were determined experimentally for PPG-425 + anisole, PPG-425 + PEGME-350, and the polymer blends of PPG-425 + PEGME-350 and PEG-200 + PPG-425 with anisole. The $P-V-T$ data of the constituent binaries were correlated with the Flory–Orwoll–Vrij (FOV) and the Schotte equations of state (EOS) while the binary interaction parameters of the equations were determined. These binary parameters were

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Table 1
Comparison of experimental results with literature values for PPG-425

T (K)	P (MPa)	ρ (g cm^{-3})	
		This work	Literature[a]
298.15	0.1	1.0031	1.0025
	10	1.0090	1.0086
	20	1.0149	1.0145
	30	1.0203	1.0200
318.15	0.1	0.9872	0.9866
	10	0.9938	0.9932
	20	1.0001	0.9996
	30	1.0059	1.0055

[a] Data source: Chang et al. [10].

in turn utilized to verify the validity of both EOS for the prediction of the $P-V-T$ behavior of the ternary polymer solutions. The new experimental results also complement information on volumetric properties for the associated polymer solutions in response to the effects of temperature, pressure, and composition.

2. Experimental section

Anisole (99 + %) and the fractionation cuts of PPG-425, PEG-200, and PEGME-350 were purchased from Aldrich Chemical Company, USA. The number-average molecular weights (M_n) and the poly-dispersities (M_w/M_n) are approximately 486 and 1.0343 for PPG-425, 260 and 1.0742 for PEG-200, and 366 and 1.0188 for PEGME-350. These values were measured with a Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF). Each substance was degassed by heat accompanying with agitation before use. The schematic diagram of the $P-V-T$ apparatus has been illustrated by Lee et al. [12] Liquid mixture sample was prepared from the degassed compounds by mass to an accuracy of ± 0.0001 in mass fraction. The density was measured with a high-pressure densitometer (DMA 512 P, Anton Paar). Pressure in the measuring cell was manipulated by a hand pump and monitored by a pressure transducer (Model-PDCR 911, 0–70 MPa, Druck) with a digital indicator (model-DPI 261, Druck). Pressure measurements were accurate to $\pm 0.1\%$ as pressures higher than atmospheric. A thermostatic bath with circulating water maintained the temperature of the measuring cell to within ± 0.03 K. A precision digital thermometer (model-1506, Hart Scientific) incorporated with an RTD platinum 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 indicated by a densimeter of DMA 48 (Anton Paar) which 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

Table 2
Experimental results for PPG-425 (1) + anisole (2)

P (MPa)	298.15 K ρ (g cm^{-3})	318.15 K	348.15 K	298.15 K ρ (g cm^{-3})	318.15 K	348.15 K
	$w_1 = 0.0$ ($x_1 = 0.0$)			$w_1 = 0.3041$[a] ($x_1 = 0.0886$)[b]		
0.1	0.9887	0.9700	0.9409	0.9917	0.9736	0.9460
10	0.9951	0.9770	0.9493	0.9981	0.9805	0.9542
15	0.9981	0.9803	0.9533	1.0012	0.9839	0.9581
20	1.0011	0.9836	0.9571	1.0042	0.9873	0.9618
25	1.0040	0.9869	0.9607	1.0070	0.9903	0.9653
30	1.0068	0.9899	0.9643	1.0099	0.9934	0.9688
35	1.0095	0.9929	0.9677	1.0128	0.9963	0.9721
40	1.0120	0.9958	0.9711	1.0153	0.9992	0.9754
45	1.0147	0.9987	0.9743	1.0179	1.0020	0.9786
50	1.0173	1.0014	0.9774	1.0205	1.0046	0.9816
	$w_1 = 0.4956$ ($x_1 = 0.1794$)			$w_1 = 0.6275$ ($x_1 = 0.2726$)		
0.1	0.9953	0.9779	0.9511	0.9982	0.9810	0.9547
10	1.0015	0.9847	0.9591	1.0044	0.9877	0.9627
15	1.0046	0.9880	0.9630	1.0074	0.9910	0.9664
20	1.0075	0.9912	0.9667	1.0103	0.9942	0.9701
25	1.0102	0.9943	0.9701	1.0130	0.9972	0.9735
30	1.0131	0.9973	0.9736	1.0158	1.0002	0.9769
35	1.0158	1.0002	0.9769	1.0185	1.0030	0.9802
40	1.0183	1.0030	0.9801	1.0210	1.0059	0.9834
45	1.0208	1.0058	0.9832	1.0236	1.0086	0.9864
50	1.0234	1.0085	0.9862	1.0261	1.0113	0.9894
	$w_1 = 0.7238$ ($x_1 = 0.3683$)			$w_1 = 0.7972$ ($x_1 = 0.4665$)		
0.1	0.9997	0.9829	0.9571	1.0007	0.9842	0.9587
10	1.0058	0.9895	0.9649	1.0069	0.9908	0.9666
15	1.0088	0.9929	0.9686	1.0099	0.9941	0.9703
20	1.0117	0.9960	0.9722	1.0127	0.9972	0.9738
25	1.0145	0.9991	0.9757	1.0155	1.0003	0.9772
30	1.0172	1.0020	0.9790	1.0182	1.0032	0.9806
35	1.0199	1.0049	0.9822	1.0209	1.0060	0.9838
40	1.0224	1.0077	0.9855	1.0234	1.0089	0.9870
45	1.0250	1.0103	0.9885	1.0260	1.0115	0.9900
50	1.0275	1.0130	0.9914	1.0284	1.0142	0.9930
	$w_1 = 0.8550$ ($x_1 = 0.5674$)			$w_1 = 0.9017$ ($x_1 = 0.6711$)		
0.1	1.0014	0.9850	0.9600	1.0019	0.9857	0.9609
10	1.0075	0.9917	0.9677	1.0080	0.9923	0.9687
15	1.0105	0.9950	0.9714	1.0109	0.9956	0.9723
20	1.0134	0.9981	0.9749	1.0138	0.9987	0.9759
25	1.0161	1.0011	0.9784	1.0165	1.0017	0.9792
30	1.0188	1.0040	0.9817	1.0193	1.0046	0.9825
35	1.0215	1.0069	0.9848	1.0220	1.0074	0.9857
40	1.0240	1.0096	0.9880	1.0245	1.0102	0.9889
45	1.0265	1.0122	0.9910	1.0270	1.0128	0.9918
50	1.0290	1.0149	0.9939	1.0294	1.0155	0.9947
	$w_1 = 0.9402$ ($x_1 = 0.7777$)			$w_1 = 0.9725$ ($x_1 = 0.8873$)		
0.1	1.0024	0.9863	0.9617	1.0028	0.9868	0.9624
10	1.0084	0.9929	0.9694	1.0088	0.9934	0.9701
15	1.0114	0.9961	0.9731	1.0117	0.9966	0.9737
20	1.0142	0.9993	0.9766	1.0146	0.9997	0.9772
25	1.0169	1.0022	0.9799	1.0173	1.0027	0.9806
30	1.0197	1.0051	0.9833	1.0200	1.0055	0.9838
35	1.0224	1.0079	0.9863	1.0227	1.0084	0.9869
40	1.0248	1.0107	0.9895	1.0251	1.0112	0.9901
45	1.0274	1.0133	0.9925	1.0277	1.0137	0.9931
50	1.0298	1.0159	0.9953	1.0301	1.0164	0.9959

Table 2 (*continued*)

	298.15 K	318.15 K	348.15 K	298.15 K	318.15 K	348.15 K
P (MPa)	ρ ($g\ cm^{-3}$)			ρ ($g\ cm^{-3}$)		
	$w_1 = 1.0$ ($x_1 = 1.0$)					
0.1	1.0031	0.9872	0.9630			
10	1.0091	0.9938	0.9707			
15	1.0120	0.9970	0.9743			
20	1.0149	1.0001	0.9778			
25	1.0176	1.0031	0.9811			
30	1.0203	1.0059	0.9844			
35	1.0230	1.0088	0.9875			
40	1.0254	1.0116	0.9906			
45	1.0280	1.0141	0.9936			
50	1.0304	1.0167	0.9964			

[a] w_1 : mass fraction of component 1.

using the literature density data of two calibration fluids: pure water [14] and dry nitrogen [15]. The calibration was made at each temperature of interest over a pressure range 0.1–50 MPa. The calibration reproduced water densities with an average absolute deviation of 0.01% over the entire calibrated conditions. The viscosity differences between the samples and the calibration fluids might affect the accuracy of density measurement by an oscillating densitometer [16], but the effect is generally minor. The accuracy of the density measurements, without the correction of viscosity effect, was estimated to within ±0.1%.

3. Results and discussion

The experimental results of PEG-200, PEGME-350, and

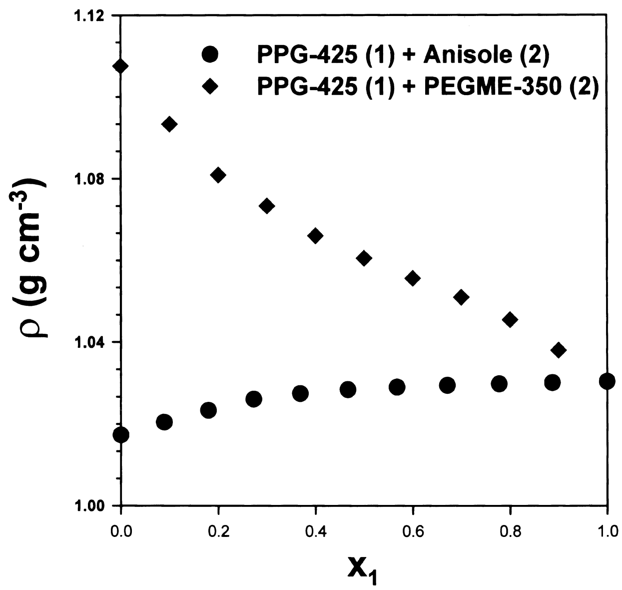

Fig. 1. Variation of density with composition for PPG-425 (1) + anisole (2) and PPG-425 (1) + PEGME-350 (2) at 298.15 K and 50 MPa.

Table 3
Experimental results for PPG-425 (1) + PEGME-350 (2)

	298.15 K	318.15 K	348.15 K	298.15 K	318.15 K	348.15 K
P (MPa)	ρ ($g\ cm^{-3}$)			ρ ($g\ cm^{-3}$)		
	$w_1 = 0.0$ ($x_1 = 0.0$)			$w_1 = 0.1286$[a] ($x_1 = 0.1000$)[b]		
0.1	1.0843	1.0671	1.0421	1.0695	1.0522	1.0271
10	1.0892	1.0728	1.0482	1.0746	1.0581	1.0335
15	1.0918	1.0755	1.0513	1.0771	1.0608	1.0366
20	1.0941	1.0780	1.0543	1.0796	1.0635	1.0397
25	1.0965	1.0807	1.0572	1.0820	1.0662	1.0426
30	1.0988	1.0831	1.0600	1.0844	1.0686	1.0455
35	1.1010	1.0855	1.0627	1.0866	1.0711	1.0482
40	1.1032	1.0879	1.0654	1.0889	1.0735	1.0510
45	1.1054	1.0902	1.0680	1.0911	1.0759	1.0536
50	1.1076	1.0925	1.0704	1.0934	1.0782	1.0561
	$w_1 = 0.2492$ ($x_1 = 0.2000$)			$w_1 = 0.3627$ ($x_1 = 0.3000$)		
0.1	1.0564	1.0394	1.0144	1.0481	1.0310	1.0059
10	1.0618	1.0453	1.0210	1.0535	1.0371	1.0127
15	1.0644	1.0481	1.0242	1.0562	1.0399	1.0160
20	1.0669	1.0508	1.0273	1.0588	1.0427	1.0193
25	1.0694	1.0535	1.0303	1.0613	1.0455	1.0223
30	1.0718	1.0560	1.0333	1.0639	1.0480	1.0253
35	1.0741	1.0585	1.0361	1.0663	1.0506	1.0282
40	1.0764	1.0610	1.0389	1.0687	1.0531	1.0311
45	1.0787	1.0633	1.0417	1.0710	1.0554	1.0338
50	1.0809	1.0657	1.0443	1.0733	1.0579	1.0365
	$w_1 = 0.4696$ ($x_1 = 0.4000$)			$w_1 = 0.5704$ ($x_1 = 0.5000$)		
0.1	1.0410	1.0240	0.9993	1.0350	1.0183	0.9936
10	1.0463	1.0301	1.0061	1.0405	1.0245	1.0006
15	1.0491	1.0330	1.0094	1.0433	1.0275	1.0040
20	1.0517	1.0357	1.0127	1.0459	1.0303	1.0073
25	1.0541	1.0385	1.0157	1.0483	1.0332	1.0103
30	1.0567	1.0410	1.0187	1.0509	1.0358	1.0134
35	1.0591	1.0436	1.0216	1.0533	1.0385	1.0163
40	1.0614	1.0461	1.0245	1.0557	1.0411	1.0193
45	1.0637	1.0485	1.0272	1.0582	1.0435	1.0220
50	1.0660	1.0509	1.0298	1.0605	1.0460	1.0247
	$w_1 = 0.6658$ ($x_1 = 0.6000$)			$w_1 = 0.7560$ ($x_1 = 0.7000$)		
0.1	1.0296	1.0131	0.9885	1.0247	1.0082	0.9831
10	1.0352	1.0194	0.9957	1.0304	1.0146	0.9904
15	1.0380	1.0225	0.9991	1.0333	1.0177	0.9938
20	1.0408	1.0255	1.0024	1.0360	1.0207	0.9972
25	1.0433	1.0283	1.0056	1.0386	1.0236	1.0004
30	1.0459	1.0310	1.0088	1.0413	1.0263	1.0035
35	1.0485	1.0338	1.0117	1.0438	1.0291	1.0065
40	1.0509	1.0364	1.0148	1.0462	1.0317	1.0095
45	1.0533	1.0388	1.0176	1.0487	1.0342	1.0124
50	1.0556	1.0413	1.0204	1.0509	1.0367	1.0152
	$w_1 = 0.8416$ ($x_1 = 0.8000$)			$w_1 = 0.9228$ ($x_1 = 0.9000$)		
0.1	1.0188	1.0023	0.9774	1.0109	0.9947	0.9701
10	1.0246	1.0087	0.9848	1.0169	1.0012	0.9776
15	1.0275	1.0119	0.9883	1.0198	1.0045	0.9812
20	1.0303	1.0149	0.9917	1.0226	1.0075	0.9846
25	1.0329	1.0178	0.9950	1.0253	1.0104	0.9879
30	1.0356	1.0206	0.9982	1.0280	1.0133	0.9912
35	1.0381	1.0233	1.0012	1.0307	1.0161	0.9942
40	1.0406	1.0261	1.0043	1.0331	1.0189	0.9974
45	1.0430	1.0286	1.0072	1.0356	1.0214	1.0002
50	1.0454	1.0311	1.0100	1.0380	1.0240	1.0031

[a] w_1 : mass fraction of component 1.
[b] x_1 : mole fraction of component 1; calculated with the molecular weights of 486 and 366 for PPG-425 and PEGME-350, respectively.

Table 4
Density at 0.1 MPa (ρ_0) and correlated results of the Tait equation for PPG-425 (1) + anisole (2)

T (K)	w_1[a]	x_1[b]	ρ_0 (g cm^{-3})	C	D (MPa)	10^5 π[c]
298.15	0.0	0.0	0.9887	0.08201	122.10	3.0
	0.3041	0.0886	0.9917	0.07999	117.80	3.3
	0.4956	0.1794	0.9953	0.08396	129.30	2.5
	0.6275	0.2726	0.9982	0.08533	133.10	2.5
	0.7238	0.3683	0.9997	0.08645	135.90	2.3
	0.7972	0.4665	1.0007	0.08067	126.00	2.2
	0.8550	0.5674	1.0014	0.08271	130.50	2.7
	0.9017	0.6711	1.0019	0.08380	133.09	3.8
	0.9402	0.7777	1.0024	0.08237	130.90	3.3
	0.9725	0.8873	1.0028	0.08205	130.60	2.7
	1.0	1.0	1.0031	0.08136	129.40	2.7
318.15	0.0	0.0	0.9700	0.08849	117.30	2.6
	0.3041	0.0886	0.9736	0.08107	107.10	4.3
	0.4956	0.1794	0.9779	0.08709	119.30	1.6
	0.6275	0.2726	0.9810	0.08258	114.00	2.0
	0.7238	0.3683	0.9829	0.08291	115.50	3.0
	0.7972	0.4665	0.9842	0.08366	117.70	2.9
	0.8550	0.5674	0.9850	0.08055	112.80	2.1
	0.9017	0.6711	0.9857	0.08255	116.80	2.4
	0.9402	0.7777	0.9863	0.07950	112.50	2.7
	0.9725	0.8873	0.9868	0.08097	115.20	2.7
	1.0	1.0	0.9872	0.07782	110.20	2.8
348.15	0.0	0.0	0.9409	0.08640	92.20	1.4
	0.3041	0.0886	0.9460	0.08500	93.50	2.9
	0.4956	0.1794	0.9511	0.08353	93.80	1.9
	0.6275	0.2726	0.9547	0.08342	95.50	1.4
	0.7238	0.3683	0.9571	0.08474	98.60	1.6
	0.7972	0.4665	0.9587	0.08267	96.40	2.1
	0.8550	0.5674	0.9600	0.08125	95.32	2.4
	0.9017	0.6711	0.9609	0.08006	94.41	2.8
	0.9402	0.7777	0.9617	0.07908	93.53	2.5
	0.9725	0.8873	0.9624	0.08094	96.82	3.2
	1.0	1.0	0.9630	0.08039	96.41	1.9

[a] w_1 : mass fraction of component 1.
[b] x_1 : mole fraction of component 1; calculated with the molecular weights of 486 and 108.14 for PPG-425 and anisole, respectively.
[c] π defines as in Eq. (3) and nine data points (n) were used to determine the values of C and D for each case.

Table 5
Density at 0.1 MPa (ρ_0) and correlated results of the Tait equation for PPG-425 (1) + PEGME-350 (2)

T (K)	w_1[a]	x_1[b]	ρ_0 (g cm^{-3})	C	D (MPa)	10^5 π[c]
298.15	0.0	0.0	1.0843	0.09442	200.10	2.9
	0.1286	0.1	1.0695	0.09547	193.80	3.0
	0.2492	0.2	1.0564	0.07932	151.10	2.4
	0.3627	0.3	1.0481	0.09778	182.70	3.2
	0.4696	0.4	1.0410	0.08751	161.90	2.9
	0.5704	0.5	1.0350	0.08938	161.50	3.9
	0.6658	0.6	1.0296	0.09166	161.60	3.9
	0.7560	0.7	1.0247	0.08246	140.80	3.0
	0.8416	0.8	1.0188	0.07742	128.00	2.3
	0.9228	0.9	1.0109	0.07858	126.80	2.7
	1.0	1.0	1.0031	0.08136	129.40	2.7
318.15	0.0	0.0	1.0671	0.07230	129.60	4.0
	0.1286	0.1	1.0522	0.07124	123.80	3.9
	0.2492	0.2	1.0394	0.06966	117.40	2.3
	0.3627	0.3	1.0310	0.07130	116.60	3.2
	0.4696	0.4	1.0240	0.07113	115.30	3.2
	0.5704	0.5	1.0183	0.07646	120.50	3.0
	0.6658	0.6	1.0131	0.07474	113.80	3.2
	0.7560	0.7	1.0082	0.07398	110.60	1.9
	0.8416	0.8	1.0023	0.07955	118.40	2.8
	0.9228	0.9	0.9947	0.07862	113.40	3.5
	1.0	1.0	0.9872	0.07782	110.20	2.8
348.15	0.0	0.0	1.0421	0.08770	141.00	5.0
	0.1286	0.1	1.0271	0.08319	127.20	3.0
	0.2492	0.2	1.0144	0.08595	126.00	2.2
	0.3627	0.3	1.0059	0.08080	113.30	3.1
	0.4696	0.4	0.9993	0.08211	114.40	2.9
	0.5704	0.5	0.9936	0.07954	107.10	2.4
	0.6658	0.6	0.9885	0.08347	109.80	2.5
	0.7560	0.7	0.9831	0.08185	106.00	2.2
	0.8416	0.8	0.9774	0.08307	104.80	2.2
	0.9228	0.9	0.9701	0.08054	98.80	2.8
	1.0	1.0	0.9630	0.08039	96.41	1.9

[a] w_1 : mass fraction of component 1.
[b] x_1 : mole fraction of component 1; calculated with the molecular weights of 486 and 366 for PPG-425 and PEGME-350, respectively.
[c] π defines as in Eq. (3) and nine data points (n) were used to determine the values of C and D for each case.

anisole have been compared with literature values in Lee et al. [12] Table 1 compares the measured densities of PPG-425 with literature values, indicating that the agreement is within the uncertainty of the measurements. Tables 2 and 3 list the experimental results, over a temperature range of 298.15 to 348.15 K and pressures up to 50 MPa, for polymer solutions of PPG-425 + anisole and polymer blends of PPG-425 + PEGME-350, respectively. Fig. 1 shows the variation of densities with composition for these two binary systems at 298.15 K and 50 MPa.

The pressure effect on the isothermal densities of a given composition is represented accurately by 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):

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

where n is the number of data points. $\rho_{k,\mathrm{calc}}$ and $\rho_{k,\mathrm{expt}}$ refer to the calculated and the experimental densities for the kth point, respectively. Tables 4 and 5 report the calculated results, including the values of ρ_0, C, D, and π for PPG-425 + anisole and PPG-425 + PEGME-350, respectively. With these tabulated ρ_0, C, and D, the Tait equation reproduces the densities at pressures higher than 0.1 MPa to within the experimental uncertainty.

By assuming that the isothermal bulk modulus linearly depends on pressure, $1/\kappa_T = 1/\kappa_{T_0} + \delta(P - 0.1)$, the P–V–T data of polymers, solvents, and solutions could

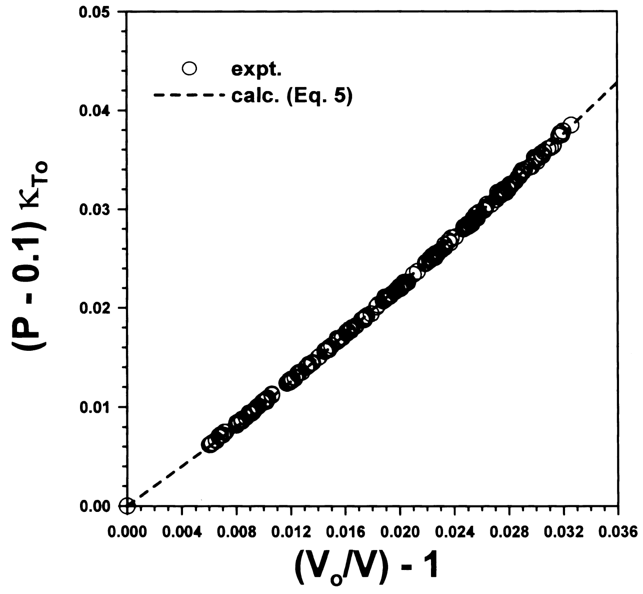

Fig. 2. Generalized correlation of the $P-V-T$ data for PPG-425 (1) + anisole (2) at different compositions.

be represented by a generalized equation [17]:

$$(P - 0.1)\kappa_{T_0} = \frac{1}{\delta}\left[\left(\frac{V_0}{V}\right)^{\delta} - 1\right] \tag{4}$$

where κ_{T_0} and V_0 are the isothermal compressibility and the specific volume at 0.1 MPa, respectively, and δ is a characteristic parameter. Lin et al. [13] found that all the $P-V-T$ data of a polymer solution system were also merged onto a single curve of $(P - 0.1)\ \kappa_{T_0}$ vs. $(V_0/V) - 1$. The relation was expressed by an empirical equation with

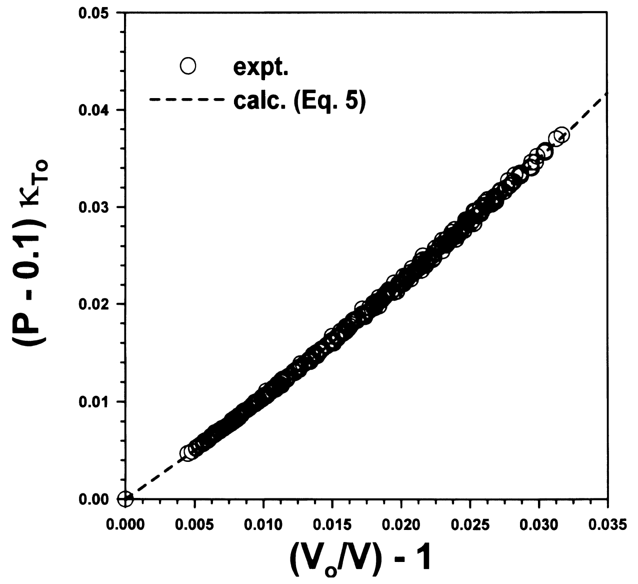

Fig. 3. Generalized correlation of the $P-V-T$ data for PPG-425 (1) + PEGME-350 (2) at different compositions.

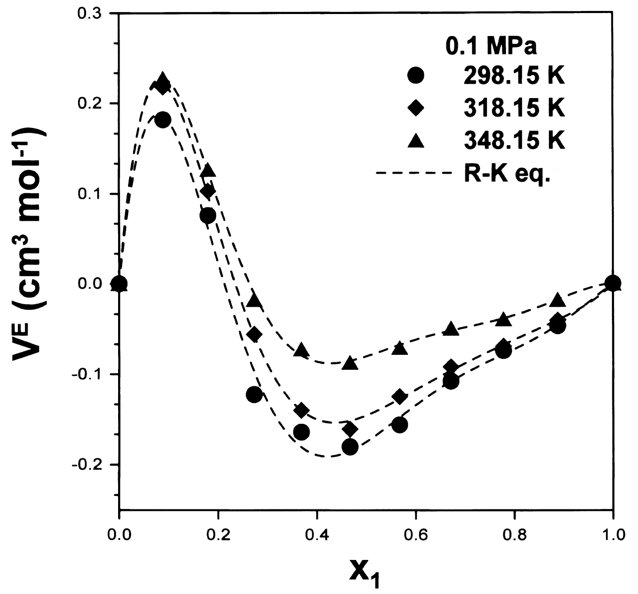

Fig. 4. Variations of excess volume with composition for PPG-425 (1) + anisole (2) at 0.1 MPa.

two characteristic parameters, δ_1 and δ_2:

$$(P - 0.1)\kappa_{T_0} = \delta_1\left(\frac{V_0}{V} - 1\right)^{\delta_2} \tag{5}$$

Figs. 2 and 3 are the illustrations for PPG-425 + anisole and PPG-425 + PEGME-350, respectively, in which the dashed curves are the correlated results from Eq. (5). In the data correlation, κ_{T_0} at given temperature and composition were calculated from its definition with the aid of the Tait equation:

$$\kappa_{T_0} = \frac{C}{D + 0.1} \tag{6}$$

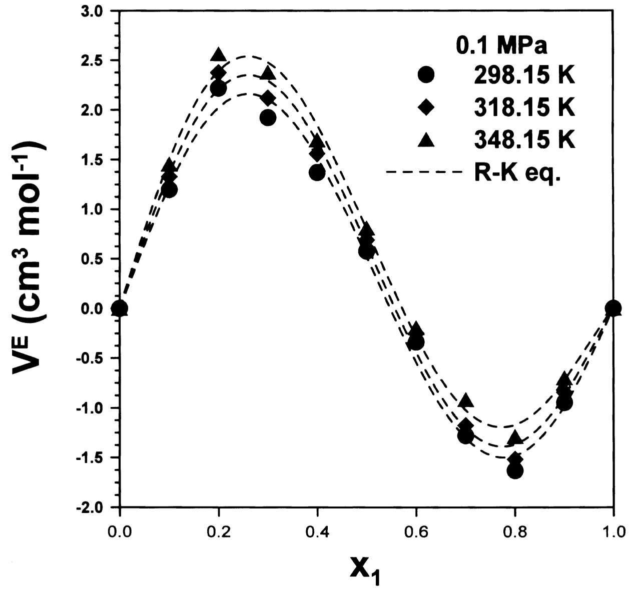

Fig. 5. Variations of excess volume with composition for PPG-425 (1) + PEGME-350 (2) at 0.1 MPa.

Table 6
Correlated results of the Redlich–Kister equation for PPG-425 (1) + anisole (2) and PPG-425 (1) + PEGME-350 (2)

T (K)	P (MPa)	A_0	A_1	A_2	A_3	A_4	A_5	AAD[a] ($cm^3 mol^{-1}$)
PPG-425 (1) + Anisole (2)								
298.15	0.1	−0.7233	0.5544	0.9615	−2.7640	2.0865	−0.7704	0.0055
	10	−0.7697	0.4557	1.3582	−2.8008	1.3519	–	0.0073
	15	−0.7592	0.3945	1.4838	−2.5341	0.9153	–	0.0074
	20	−0.7586	0.3608	1.4532	−2.4123	0.9298	–	0.0058
	25	−0.7800	0.4244	1.6413	−2.4770	0.6894	–	0.0071
	30	−0.7454	0.2543	1.2957	−2.0370	0.9518	–	0.0094
	35	−0.7769	0.1821	1.7267	−1.7494	0.1314	–	0.0104
	40	−0.7723	0.2416	1.6371	−1.8059	0.2325	–	0.0114
	45	−0.7854	0.2815	1.8072	−1.8261	−0.0514	–	0.0123
	50	−0.8369	0.2533	2.0497	−1.7321	−0.2820	–	0.0121
318.15	0.1	−0.6012	0.3143	0.9410	−2.2244	2.3679	−1.5588	0.0057
	10	−0.5789	0.3800	0.9224	−3.0048	2.2182	–	0.0068
	15	−0.6068	0.4538	1.1636	−3.0738	1.8426	–	0.0054
	20	−0.5989	0.2853	1.2359	−2.5075	1.3467	–	0.0067
	25	−0.6249	0.4474	1.4747	−2.9109	1.3730	–	0.0065
	30	−0.5803	0.3587	1.0176	−2.6235	1.8344	–	0.0047
	35	−0.6104	0.3231	1.2270	−2.5162	1.5918	–	0.0064
	40	−0.6108	0.3316	1.3488	−2.4751	1.3476	–	0.0038
	45	−0.6355	0.3502	1.1384	−2.6655	1.6088	–	0.0062
	50	−0.6696	0.4377	1.1010	−2.8958	1.8609	–	0.0078
348.15	0.1	−0.3206	0.3528	0.1794	−2.3593	3.3403	−1.2308	0.0027
	10	−0.3800	0.1210	0.6207	−1.4542	2.3347	−1.9695	0.0057
	15	−0.3855	0.1085	0.4078	−1.2570	2.6942	−2.1107	0.0059
	20	−0.3510	0.1253	0.2187	−1.0763	2.9433	−2.3105	0.0039
	25	−0.4203	0.1347	0.5823	−0.8325	2.5925	−2.6723	0.0032
	30	−0.4237	0.1324	0.5469	−0.8459	2.7506	−2.4758	0.0075
	35	−0.4080	0.1809	0.4714	−1.3970	2.8982	−1.8285	0.0078
	40	−0.4532	0.4969	0.7908	−3.2198	2.3301	–	0.0092
	45	−0.4232	0.4657	0.5510	−2.9699	2.0164	–	0.0062
	50	−0.4716	0.5008	0.6856	−3.0270	2.4753	–	0.0073
PPG-425 (1) + PEGME-350 (2)								
298.15	0.1	2.0775	−21.9103	−1.0698	10.2162	–	–	0.1148
	10	2.1514	−21.4262	−1.3766	9.6713	–	–	0.1106
	15	2.2196	−21.0591	−1.5048	9.0274	–	–	0.1084
	20	2.2092	−21.0012	−1.3501	9.1261	–	–	0.1071
	25	2.2309	−20.8680	−1.5170	8.8952	–	–	0.1119
	30	2.2498	−20.5580	−1.3907	8.6359	–	–	0.1123
	35	2.2898	−20.3714	−1.5217	8.3094	–	–	0.1089
	40	2.2437	−20.2901	−1.3439	8.4736	–	–	0.1084
	45	2.1932	−20.2207	−1.1828	8.5878	–	–	0.1090
	50	2.2293	−19.9557	−1.3307	8.2381	–	–	0.1117
318.15	0.1	2.5673	−22.5492	0.1369	10.9896	–	–	0.1048
	10	2.6290	−22.4673	−0.1433	11.4002	–	–	0.1031
	15	2.7238	−22.4224	−0.3051	11.2214	–	–	0.0943
	20	2.7575	−22.2068	−0.2559	11.0398	–	–	0.0912
	25	2.7812	−22.1690	−0.3533	11.0443	–	–	0.0875
	30	2.8364	−22.2191	−0.3172	11.2746	–	–	0.0832
	35	2.8734	−22.1990	−0.4177	11.2542	–	–	0.0786
	40	2.9076	−22.0564	−0.5402	10.9983	–	–	0.0759
	45	2.9633	−22.0391	−0.7424	11.0958	–	–	0.0781
	50	2.9882	−21.9300	−0.6689	11.1435	–	–	0.0773
348.15	0.1	3.1888	−22.6434	1.7089	11.3912	–	–	0.0896
	10	3.2669	−22.1896	1.4686	11.2060	–	–	0.0811
	15	3.2574	−21.8926	1.5357	10.8168	–	–	0.0863
	20	3.2590	−21.7103	1.6451	10.7321	–	–	0.0855
	25	3.2836	−21.4096	1.6535	10.3808	–	–	0.0888
	30	3.2965	−21.1974	1.5632	10.0413	–	–	0.0792

Table 6 (*continued*)

T (K)	P (MPa)	A_0	A_1	A_2	A_3	A_4	A_5	AAD[a] (cm^3 mol^{-1})
	35	3.3113	−21.0662	1.5894	10.0357	–	–	0.0824
	40	3.3176	−20.7924	1.4714	9.5477	–	–	0.0780
	45	3.3532	−20.8546	1.5087	10.0200	–	–	0.0734
	50	3.2991	−20.5851	1.6763	9.5865	–	–	0.0758

[a] AAD (cm^3 mol^{-1}) $= (1/n)\sum_{k=1}^{n} |V^{\mathrm{E}}_{k,\mathrm{calc}} - V^{\mathrm{E}}_{k,\mathrm{expt}}|$, where n is the number of data points and V^{E} is the molar excess volume.

and the Tait constants C and D were taken from Tables 4 and 5. The empirical model, Eq. (5), correlates density (ρ) data to an absolute average deviation (AAD) of 0.013% (with $\delta_1 = 1.7473$ and $\delta_2 = 1.1156$) for PPG-425 + anisole and 0.016% (with $\delta_1 = 1.6570$ and $\delta_2 = 1.1008$) for PPG-425 + PEGME-350. Consequently the characteristic parameters δ_1 and δ_2 may be determined from few points of experimental data (in principle, two points will be sufficient) of any given composition including those of the pure constituent compounds. Once the parameters are determined, Eq. (5) can be used for estimation of the density at elevated pressures from the knowledge at atmospheric pressure (or other reference pressure), κ_{T_0} and V_0.

The volume change of mixing or excess volume (V^{E}) is related to the molecular interactions in a mixture. By definition, the excess volumes of a binary system are calculated from the following equation:

$$V^{\mathrm{E}} = V_{\mathrm{m}} - x_1V_1^0 - x_2V_2^0 \tag{7}$$

with

$$V_{\mathrm{m}} = \frac{x_1M_1 + x_2M_2}{\rho} \tag{8}$$

where V_{m} is the molar volume of a mixture. x_i, V_i^0, and M_i are the mole fraction, molar volume, and molecular weight, respectively, for component i. The uncertainty of the calculated excess volumes was estimated to be about ± 0.05 cm^3 mol^{-1}.

The excess volumes at 0.1 MPa varying with composition are s-shaped as shown in Fig. 4 for PPG-425 + anisole.

Table 7
Experimental results for PPG-425 (1) + PEGME-350 (2) + anisole (3)

P (MPa)	298.15 K	318.15 K	348.15 K	298.15 K	318.15 K	348.15 K
	ρ (g cm^{-3})			ρ (g cm^{-3})		
	w_1, w_2 = 0.2872, 0.6489 ($x_1, x_2 = 0.2, 0.6$)			$w_1, w_2 = 0.4131, 0.3111$[a] ($x_1, x_2 = 0.2, 0.2$)[b]		
0.1	1.0546	1.0376	1.0126	1.0285	1.0112	0.9852
10	1.0599	1.0437	1.0194	1.0341	1.0176	0.9926
15	1.0626	1.0465	1.0226	1.0369	1.0207	0.9961
20	1.0652	1.0499	1.0258	1.0396	1.0236	0.9995
25	1.0677	1.0521	1.0289	1.0422	1.0265	1.0028
30	1.0702	1.0547	1.0319	1.0449	1.0293	1.0060
35	1.0726	1.0573	1.0348	1.0474	1.0320	1.0091
40	1.0749	1.0598	1.0376	1.0498	1.0347	1.0121
45	1.0772	1.0623	1.0403	1.0522	1.0373	1.0150
50	1.0795	1.0647	1.0430	1.0546	1.0398	1.0178
	w_1, w_2 = 0.7546, 0.1894 (x_1, x_2 = 0.6, 0.2)			$w_1, w_2 = 0.5247, 0.3669$ (x_1, x_2 = 0.35, 0.325)		
0.1	1.0164	0.9998	0.9749	1.0334	1.0168	0.9916
10	1.0223	1.0064	0.9823	1.0390	1.0231	0.9989
15	1.0252	1.0094	0.9858	1.0413	1.0261	1.0023
20	1.0280	1.0125	0.9892	1.0444	1.0290	1.0056
25	1.0306	1.0154	0.9924	1.0470	1.0318	1.0088
30	1.0333	1.0183	0.9956	1.0496	1.0345	1.0120
35	1.0359	1.0210	0.9986	1.0521	1.0372	1.0149
40	1.0383	1.0238	1.0016	1.0545	1.0399	1.0179
45	1.0408	1.0263	1.0045	1.0568	1.0423	1.0208
50	1.0432	1.0289	1.0072	1.0591	1.0448	1.0235

[a] w_1, w_2 : mass fractions of components 1 and 2, respectively.
[b] x_1, x_2: mole fractions of components 1 and 2, respectively; calculated with the molecular weights of 486, 366, and 108.14 for PPG-425, PEGME-350, and anisole, respectively.

Table 8
Experimental results for PEG-200 (1) + PPG-425 (2) + anisole (3)

P (MPa)	298.15 K	318.15 K	348.15 K	298.15 K	318.15 K	348.15 K
	ρ (g cm^{-3})			ρ (g cm^{-3})		
	w_1, w_2 = 0.1424, 0.7984 ($x_1, x_2 = 0.2, 0.6$)			$w_1, w_2 = 0.2429, 0.4540$[a] ($x_1, x_2 = 0.2, 0.2$)[b]		
0.1	1.0168	1.0005	0.9757	1.0261	1.0090	0.9827
10	1.0226	1.0069	0.9831	1.0318	1.0153	0.9900
15	1.0254	1.0100	0.9866	1.0346	1.0183	0.9935
20	1.0281	1.0130	0.9899	1.0372	1.0213	0.9970
25	1.0308	1.0159	0.9932	1.0399	1.0241	1.0002
30	1.0335	1.0187	0.9963	1.0425	1.0269	1.0033
35	1.0360	1.0215	0.9993	1.0450	1.0296	1.0064
40	1.0384	1.0242	1.0023	1.0474	1.0323	1.0094
45	1.0409	1.0267	1.0052	1.0498	1.0349	1.0123
50	1.0432	1.0293	1.0080	1.0522	1.0374	1.0151
	w_1, w_2 = 0.5676, 0.3537 (x_1, x_2 = 0.6, 0.2)			$w_1, w_2 = 0.3203, 0.6000$ (x_1, x_2 = 0.35, 0.325)		
0.1	1.0667	1.0502	1.0243	1.0364	1.0197	0.9948
10	1.0716	1.0559	1.0305	1.0419	1.0260	1.0018
15	1.0739	1.0585	1.0334	1.0446	1.0290	1.0052
20	1.0763	1.0611	1.0364	1.0472	1.0319	1.0085
25	1.0785	1.0636	1.0391	1.0497	1.0347	1.0116
30	1.0809	1.0661	1.0418	1.0522	1.0374	1.0146
35	1.0831	1.0685	1.0444	1.0547	1.0400	1.0175
40	1.0852	1.0709	1.0471	1.0570	1.0426	1.0204
45	1.0873	1.0731	1.0495	1.0593	1.0450	1.0232
50	1.0893	1.0754	1.0520	1.0615	1.0475	1.0259

[a] w_1, w_2 : mass fractions of components 1 and 2, respectively.
[b] x_1, x_2 : mole fractions of components 1 and 2, respectively; calculated with the molecular weights of 260, 486, and 108.14 for PEG-200, PPG-425, and anisole, respectively.

Table 9
Results of specific volume correlation with the equations of state for 'pure' compounds

Compound	FOV EOS				Schotte EOS			
	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]
PPG-425	537.85	5988.1	0.8282	0.00025	545.83	5371.6	0.8196	0.00025
PEG-200	725.05	6485.7	0.7551	0.00023	767.36	5741.8	0.7449	0.00017
PEGME-350	686.19	6100.8	0.7695	0.00021	702.07	5393.1	0.7589	0.00014
Anisole	640.23	5363.4	0.8164	0.00024	651.30	4752.9	0.8058	0.00025

[a] AAD (cm^3 g^{-1}) $= (1/n)\sum_{k=1}^{n} |V_{k,\mathrm{calc}} - V_{k,\mathrm{expt}}|$, where V is the specific volume.

Positive excess volumes exhibit in the solvent-rich region (mole fraction of PPG-425 up to about 0.25), whereas the V^E values change into negative as increasing the mole fraction of PPG-425. Similar behavior is also found in the polymer blends of PPG-425 and PEGME-350 as shown in Fig. 5. The degree of volume expansion (positive excess volume) increases with increasing temperature, while the volume contraction (negative excess volume) decreases with an increase of temperature. The excess volumes are correlated with the Redlich–Kister equation:

$$V^E = x_1 x_2 \sum_{k=0}^{n_k} A_k (x_1 - x_2)^k \tag{9}$$

Table 6 gives the correlated results. The curves in Figs. 4 and 5 are the calculated results from this equation.

The volumetric properties of ternary systems, polymer blends with a solvent, are also measured. Tables 7 and 8 report the experimental results for the polymer blends of PPG-425 + PEGME-350 and PEG-200 + PPG-425 with anisole, respectively. These data have served as a basis for testing the validity of polymer equations of state for predicting the volumetric properties of multicomponent systems.

4. *P–V–T* calculations with equations of state

In the present study, the experimental specific volumes were correlated with two polymer EOS: the FOV [18] and the Schotte [19]. These EOS were expressed as follows.

Table 10
Results of specific volume correlation with the equations of state for binary polymer solutions

Mixture (1) + (2)	FOV EOS		Schotte EOS	
	Δ_{12}	AAD[a] (%)	Δ_{12}	AAD[a] (%)
PPG-425 + anisole	−0.0142	0.047	−0.0127	0.052
PEG-200 + anisole[b]	−0.0299	0.150	−0.0317	0.140
PEGME-350 + anisole[b]	−0.1294	0.220	−0.1290	0.210
PPG-425 + PEGME-350	−0.0048	0.264	−0.0036	0.255
PPG-400 + PEG-200[c]	−0.0004	0.146	−0.0579	0.115

[a] AAD (%) $= (100/n)\sum_{k=1}^{n} |V_{k,calc} - V_{k,\mathrm{expt}}|/V_{k,\mathrm{expt}}$.
[b] Data source: Lee et al. [12].
[c] Data source: Colin et al. [7].

The FOV EOS:

$$\frac{\overline{P}\,\overline{V}}{\overline{T}} = \frac{\overline{V}^{1/3}}{\overline{V}^{1/3} - 1} - \frac{1}{\overline{T}\,\overline{V}} \tag{10}$$

The Schotte EOS:

$$\frac{\overline{P}\,\overline{V}}{\overline{T}} = \frac{RT^*}{P^* M V^*}\left(1 - \frac{1}{\overline{V}^{1/3}}\right) + \frac{1}{\overline{V}^{1/3} - 1} - \frac{1}{\overline{T}\,\overline{V}} \tag{11}$$

where M is the molecular weight, $\overline{P} = P/P^*$, $\overline{V} = V/V^*$, and $\overline{T} = T/T^*$. Each EOS contains three parameters P^*, V^*, and T^*, which are characteristic pressure, specific volume, and temperature, respectively. The values of parameters were determined by fitting the EOS to experimental $P–V–T$ data for each component. Table 9 presents the correlated results for PPG-425, PEG-200, PEGME-350, and anisole. The tabulated characteristic parameters are further applied to calculate the specific volumes of the polymer solutions and the polymer blends via the following mixing rules [19]:

$$V_m^* = \left[M_m\left(\sum_{i=1}^{c} \frac{\Psi_i}{M_i V_i^*}\right)\right]^{-1} \tag{12}$$

$$T_m^* = \frac{P_m^*}{\sum_{i=1}^{c} \frac{\Psi_i P_i^*}{T_i^*}} \tag{13}$$

and

$$P_m^* = \sum_{i=1}^{c}\sum_{j=1}^{c} \Psi_i \Psi_j P_{ij}^* \tag{14}$$

with

$$\Psi_i = \frac{w_i V_i^*}{\sum_{i=1}^{c} w_i V_i^*} \tag{15}$$

and

$$P_{ij}^* = (1 - \Delta_{ij})(P_i^* P_j^*)^{0.5} \tag{16}$$

where c is the number of components. 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_{ij} in Eq. (16) is a binary interaction constant for the $i–j$ pair that was determined from the $P–V–T$ data

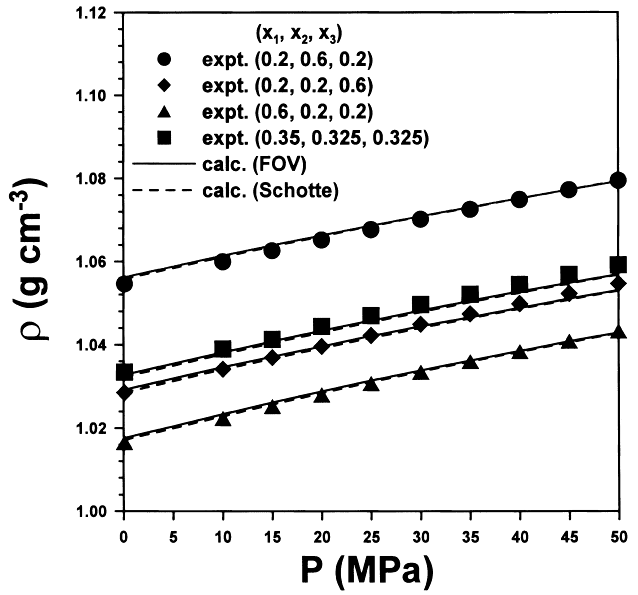

Fig. 6. Comparison of predicted densities with experimental values for ternary polymer solutions of PPG-425 (1) + PEGME-350 (2) + anisole (3) at 298.15 K.

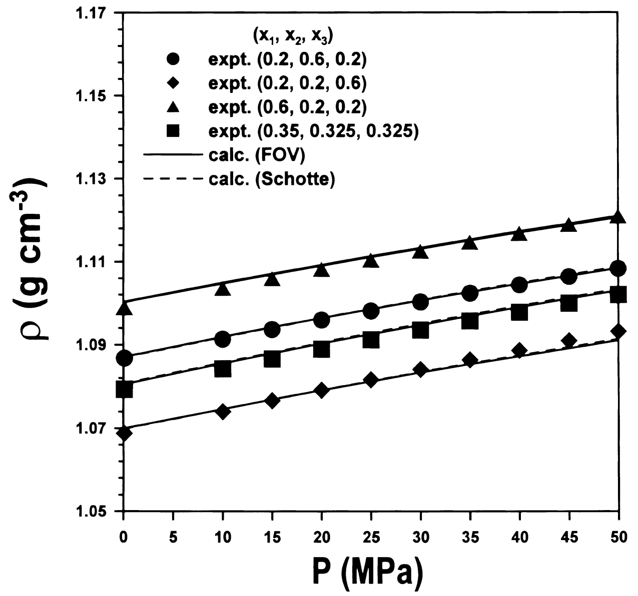

Fig. 7. Comparison of predicted densities with experimental values for ternary polymer solutions of PEG-200 (1) + PPG-425 (2) + anisole (3) at 298.15 K.

of the binary system. The calculated results are reported in Table 10. Both the FOV and the Schotte EOS represent quantitatively the $P-V-T$ behavior of the related binary systems, including PPG-425 + anisole, PEG-200 + anisole, PEGME-350 + anisole, PPG-425 + PEGME-350, PPG-400 + PEG-200 over the entire experimental conditions. By using those determined binary interaction parameters, the FOV and the Schotte EOS were employed to predict the specific volumes for the polymer blends of PPG-425 + PEGME-350 and PEG-200 + PPG-425 with anisole. Figs. 6 and 7 compare the predicted results with the experimental values for these two ternary polymeric systems at 298.15 K. Table 11 lists AAD% of the prediction, indicating that both EOS predicted the specific volume to an AAD of better than 0.13%. The prediction is accurate to about within the experimental uncertainty.

5. Conclusions

The properties of $P-V-T$ have been measured for PPG-425 + anisole, PPG-425 + PEGME-350, and polymer blends of PPG-425 + PEGME-350 and PEG-200 + PPG-425 with anisole at temperatures from 298.15 to 348.15 K and pressures up to 50 MPa. The Tait equation represented accurately the pressure effect on liquid density for these two investigated binary systems. Moreover, the $P-V-T$ data were also well correlated over the entire experimental conditions by a generalized equation with two characteristic parameters. The excess volumes of two binary systems were found to vary from positive to negative as increasing the mole fraction of PPG-425. Both the FOV and the Schotte EOS not only correlated satisfactorily the $P-V-T$ data for the related binary systems, but also predicted the specific

Table 11
Predicted results for ternary polymer solutions

Mixture (1) + (2) + (3)	x_1, x_2	AAD[a] (%)	
		FOV EOS	Schotte EOS
PPG-425 + PEGME-350 + anisole	0.2, 0.6	0.12	0.10
	0.2, 0.2	0.08	0.07
	0.6, 0.2	0.11	0.09
	0.35, 0.325	0.10	0.13
PEG-200 + PPG-425 + anisole	0.2, 0.6	0.10	0.10
	0.2, 0.2	0.08	0.09
	0.6, 0.2	0.08	0.10
	0.35, 0.325	0.07	0.10

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

volumes of ternary polymer solutions to about within experimental uncertainty.

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