Pressure−Volume−Temperature Properties for Binary Polymer Solutions of Poly(propylene glycol) with 1-Octanol and Acetophenone

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Received February 5, 2001; Revised Manuscript Received June 18, 2001

ABSTRACT: The pressure−volume−temperature ($P-V-T$) properties were measured for polymer solutions of poly(propylene glycol) + 1-octanol and poly(propylene glycol) + acetophenone at temperatures from 298 to 348 K and pressures up to 50 MPa. The experimental density data were used to calculate the excess volumes, which show a change from negative to positive as the mole fraction of the polymer component is increased for both systems. The Tait equation accurately represents the pressure effect on the liquid densities over the entire pressure range. A generalized equation with two characteristic parameters correlates well all of the $P-V-T$ data for each binary system. The experimental specific volumes were also correlated satisfactorily with the Flory−Orwoll−Vrij and the Schotte equations of state.

Introduction

Pressure−volume−temperature ($P-V-T$) data for polymer materials are fundamentally important for polymer processing and the development of polymer equations of state. The data for mixtures and their constituent compounds are often used to determine the equation constants, which are then applied to calculate other thermodynamic properties for the same mixtures at the conditions of interest. Dee et al.,[1] for example, reported the characteristic parameters of the Flory−Orwoll−Vrij (FOV) equation of state for various polymer liquids, such as polyethylene, poly(dimethyl siloxane), poly(ethylene glycol) (PEG), and poly(propylene glycol) (PPG). These parameters were obtained from $P-V-T$ data in a temperature range from room temperature to 523 K and at pressures up to 200 MPa. The specific volumes of aqueous PEGs and of oligomeric propylene glycols were measured by Muller and Rasmussen[2] and by Sandell and Goring[3] at atmospheric pressure. Earlier $P-V-T$ data for polymers have been extensively compiled by Zoller and Walsh[4] over wide ranges of temperature and pressure. The data for associated polymer solutions and polymer blends were reported recently for systems such as poly(4-hydroxystyrene) + acetone (Compostizo et al.[5]), poly(4-hydroxystyrene) + tetrahydrofuran and poly(4-hydroxystyrene) + ethanol (Compostizo et al.[6]), PPG + *n*-hexane and PPG + ethanol (Colin et al.[7]), and PEG + PPG (Colin et al.[8]). These data were employed to examine lattice-fluid equations of state[9] for describing hydrogen-bonding effects on the volumetric properties of polymer solutions. Additionally, our research group at NTUST has also made extensive $P-V-T$ measurements for polymeric materials over a temperature range from 298.15 to 338.15 K and at pressures up to 30 MPa. Lee et al.[10] 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.[11] made similar determinations for 10 fractionation cuts of PEG and PPG; and Lee et al.[12] did the same for polymer solutions of PEG-200 + 1-octanol and PEG-600 + 1-octanol. Lee et al.[13] extended the pressures up to 50 MPa for PEGME−350 + anisole and PEG-200 + anisole. As part of a continuation of these studies, $P-V-T$ properties are reported in this study for binary polymer solutions of PPG-4000 + 1-octanol and PPG-4000 + acetophenone at temperatures from 298.15 to 348.15 K and pressures up to 50 MPa. These two systems contain a common associating oligomeric compound, PPG-4000, with a strongly polar solvent. 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

1-Octanol (>99 %), acetophenone (99%), and the fractionation cuts of PPG-4000 were purchased from Aldrich Chemical Co. (Milwaukee, WI). The number-average molecular weight (M_n) and the polydispersity (M_w/M_n) are approximately 4960 and 1.008, respectively, for PPG-4000. These values were measured with a matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) technique. 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.[13] Each 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). The 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 ±0.1% at 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 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 densimeter of model DMA 48 (Anton Paar) and was converted into density (ρ_i) via

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

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10.1021/ma010204f CCC: $20.00
Published on Web 08/03/2001

Table 1. Comparison of Experimental Results with Literature Values for 1-Octanol, Acetophenone, and PPG-4000

substance	T/K	P/MPa	ρ/g cm^{-3} this work	ρ/g cm^{-3} literature	data source
1-octanol	298.15	0.1	0.8216	0.8211	Rauf and Stewart[17]
				0.8212	Sastry and Valand[18]
				0.8212	Lee et al.[12]
				0.8218	Garg et al.[19]
				0.8218	Wagner and Heintz[20]
				0.8223	TRC Tables[21]
				0.8226	Diaz Pena and Tardajos[22]
1-octanol	348.15	0.1	0.7855	0.7854	Garg et al.[19]
		10.0	0.7933	0.7931	Garg et al.[19]
acetophenone	298.15	0.1	1.0224	1.0225	Aminabhavi et al.[23]
	348.15	0.1	0.9792	0.9806	Steele et al.[24]
PPG-4000	298.15	0.1	0.9979	0.9984	Chang et al.[11]
		20.0	1.0100	1.0106	Chang et al.[11]
		30.0	1.0156	1.0160	Chang et al.[11]
	318.15	0.1	0.9828	0.9833	Chang et al.[11]
				0.9818[a]	Zoller and Walsh[4]
		20.0	0.9959	0.9967	Chang et al.[11]
				0.9938[a]	Zoller and Walsh[4]
		40.0	1.0076	1.0049[a]	Zoller and Walsh[4]

[a] Measured at 318.35 K with an accuracy of ± 0.002 cm^3 g^{-1} for specific volume.

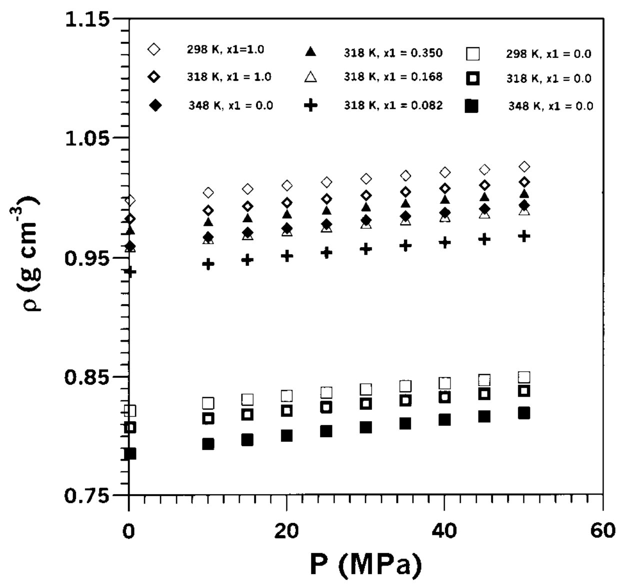

Figure 1. Variation of density with pressure for PPG-4000 (1) + 1-octanol (2).

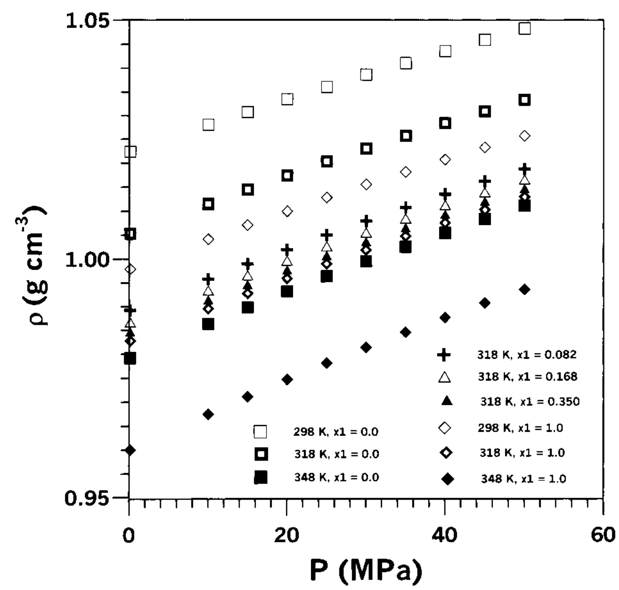

Figure 2. Variation of density with pressure for PPG-4000 (1) + acetophenone (2).

where A and B are apparatus parameters determined by using the literature $P-V-T$ data for two calibration fluids, namely, pure water[14] and dry nitrogen.[15] The calibration was made at each temperature of interest over a pressure range of 0.1−50 MPa. The calibration reproduced water densities with an average absolute deviation of 0.01% over the entire range of calibrated conditions. The viscosity differences between the samples and the calibration fluids might affect the accuracy of density measurements by an oscillating densitometer (Ashcroft et al.[16]), but the effect is generally minor. The accuracy of the density measurements, without correction for the viscosity effect, is estimated to be within ±0.1%.

Results and Discussion

Table 1 compares the experimental results with literature values for the constituent compounds. The agreement is within the uncertainty of the measurements. The results of the $P-V-T$ measurements are listed in Tables 2 and 3 for PPG + 1-octanol and PPG + acetophenone, respectively. Figures 1 and 2 show that the densities of a mixture at a given composition increase approximately linearly with increasing pressure over the investigated conditions. The effect of pressure on the isothermal density of a system with a given composition can be represented accurately by the Tait equation

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

where ρ_o 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)

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

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_o, C, D,

Table 2. Experimental Results for PPG-4000 (1) + 1-Octanol (2)

	ρ/g cm^{-3}			ρ/g cm^{-3}		
P/MPa	298.15 K	318.15 K	348.15 K	298.15 K	318.15 K	348.15 K
	$w_1 = 0.0$ ($x_1 = 0.0$)			$w_1 = 0.7734^a$ ($x_1 = 0.082$)^b		
0.1	0.8216	0.8077	0.7855	0.9534	0.9381	0.9149
10	0.8278	0.8149	0.7933	0.9596	0.9448	0.9226
15	0.8308	0.8182	0.7969	0.9626	0.9481	0.9263
20	0.8337	0.8213	0.8005	0.9654	0.9513	0.9298
25	0.8364	0.8243	0.8039	0.9682	0.9543	0.9332
30	0.8391	0.8272	0.8072	0.9709	0.9572	0.9365
35	0.8417	0.8300	0.8104	0.9736	0.9601	0.9397
40	0.8442	0.8327	0.8135	0.9762	0.9628	0.9428
45	0.8467	0.8354	0.8164	0.9787	0.9655	0.9458
50	0.8491	0.8380	0.8193	0.9812	0.9681	0.9486
	$w_1 = 0.8848$ ($x_1 = 0.168$)			$w_1 = 0.9294$ ($x_1 = 0.257$)		
0.1	0.9745	0.9593	0.9362	0.9830	0.9680	0.9451
10	0.9807	0.9659	0.9439	0.9893	0.9748	0.9529
15	0.9837	0.9692	0.9476	0.9923	0.9780	0.9566
20	0.9865	0.9724	0.9513	0.9952	0.9812	0.9601
25	0.9893	0.9755	0.9548	0.9980	0.9842	0.9636
30	0.9921	0.9785	0.9580	1.0007	0.9871	0.9668
35	0.9947	0.9813	0.9612	1.0034	0.9900	0.9700
40	0.9973	0.9841	0.9644	1.0060	0.9928	0.9731
45	0.9998	0.9869	0.9673	1.0085	0.9955	0.9761
50	1.0023	0.9895	0.9703	1.0110	0.9982	0.9790
	$w_1 = 0.9534$ ($x_1 = 0.350$)			$w_1 = 0.9685$ ($x_1 = 0.446$)		
0.1	0.9876	0.9724	0.9496	0.9906	0.9755	0.9527
10	0.9938	0.9792	0.9572	0.9968	0.9824	0.9605
15	0.9969	0.9823	0.9609	0.9998	0.9857	0.9642
20	0.9998	0.9856	0.9645	1.0027	0.9888	0.9677
25	1.0025	0.9885	0.9679	1.0055	0.9919	0.9711
30	1.0053	0.9914	0.9711	1.0082	0.9948	0.9744
35	1.0080	0.9943	0.9743	1.0108	0.9977	0.9776
40	1.0105	0.9973	0.9775	1.0135	1.0004	0.9807
45	1.0131	0.9998	0.9804	1.0160	1.0032	0.9837
50	1.0155	1.0025	0.9833	1.0184	1.0058	0.9865
	$w_1 = 0.9788$ ($x_1 = 0.547$)			$w_1 = 0.9862$ ($x_1 = 0.653$)		
0.1	0.9928	0.9776	0.9547	0.9945	0.9792	0.9563
10	0.9990	0.9844	0.9624	1.0006	0.9861	0.9640
15	1.0021	0.9877	0.9661	1.0036	0.9895	0.9677
20	1.0050	0.9909	0.9697	1.0065	0.9925	0.9712
25	1.0077	0.9940	0.9731	1.0093	0.9955	0.9746
30	1.0104	0.9969	0.9764	1.0121	0.9985	0.9779
35	1.0132	0.9998	0.9795	1.0147	1.0014	0.9811
40	1.0158	1.0024	0.9826	1.0173	1.0042	0.9842
45	1.0183	1.0053	0.9856	1.0198	1.0069	0.9872
50	1.0208	1.0080	0.9886	1.0223	1.0095	0.9901
	$w_1 = 0.9919$ ($x_1 = 0.763$)			$w_1 = 0.9964$ ($x_1 = 0.879$)		
0.1	0.9958	0.9805	0.9576	0.9967	0.9815	0.9587
10	1.0021	0.9873	0.9653	1.0029	0.9882	0.9663
15	1.0050	0.9906	0.9689	1.0058	0.9915	0.9700
20	1.0079	0.9936	0.9724	1.0087	0.9947	0.9735
25	1.0107	0.9967	0.9758	1.0116	0.9978	0.9770
30	1.0134	0.9996	0.9791	1.0143	1.0007	0.9802
35	1.0161	1.0025	0.9824	1.0169	1.0036	0.9834
40	1.0187	1.0053	0.9854	1.0195	1.0064	0.9865
45	1.0213	1.0080	0.9885	1.0220	1.0091	0.9896
50	1.0237	1.0107	0.9914	1.0245	1.0117	0.9925
	$w_1 = 1.0$ ($x_1 = 1.0$)					
0.1	0.9979	0.9828	0.9600			
10	1.0042	0.9896	0.9675			
15	1.0071	0.9928	0.9712			
20	1.0100	0.9959	0.9747			
25	1.0128	0.9990	0.9781			
30	1.0156	1.0019	0.9814			
35	1.0182	1.0048	0.9846			
40	1.0208	1.0076	0.9877			
45	1.0233	1.0103	0.9907			
50	1.0258	1.0130	0.9936			

[a] w_1 = mass fraction of component 1. [b] x_1 = mole fraction of component 1; calculated with molecular weights of 4960 and 130.231 for PPG-4000 and 1-octanol, respectively.

Table 3. Experimental Results for PPG-4000 (1) + Acetophenone (2)

	ρ/g cm^{-3}			ρ/g cm^{-3}		
P/MPa	298.15 K	318.15 K	348.15 K	298.15 K	318.15 K	348.15 K
	$w_1 = 0.0$ ($x_1 = 0.0$)			$w_1 = 0.7872^a$ ($x_1 = 0.082$)^b		
0.1	1.0224	1.0053	0.9792	1.0052	0.9892	0.9651
10	1.0281	1.0115	0.9864	1.0110	0.9958	0.9725
15	1.0308	1.0145	0.9898	1.0140	0.9990	0.9760
20	1.0335	1.0175	0.9932	1.0168	1.0020	0.9795
25	1.0361	1.0204	0.9964	1.0197	1.0051	0.9828
30	1.0387	1.0231	0.9995	1.0223	1.0079	0.9862
35	1.0411	1.0258	1.0026	1.0249	1.0107	0.9893
40	1.0436	1.0284	1.0055	1.0274	1.0135	0.9923
45	1.0460	1.0310	1.0084	1.0300	1.0162	0.9952
50	1.0483	1.0334	1.0112	1.0323	1.0188	0.9982
	$w_1 = 0.8927$ ($x_1 = 0.168$)			$w_1 = 0.9345$ ($x_1 = 0.257$)		
0.1	1.0026	0.9867	0.9632	1.0011	0.9853	0.9620
10	1.0086	0.9934	0.9708	1.0073	0.9920	0.9696
15	1.0116	0.9966	0.9745	1.0103	0.9951	0.9732
20	1.0145	0.9997	0.9779	1.0132	0.9983	0.9768
25	1.0172	1.0027	0.9813	1.0160	1.0013	0.9802
30	1.0199	1.0056	0.9846	1.0187	1.0042	0.9834
35	1.0225	1.0085	0.9878	1.0214	1.0071	0.9866
40	1.0250	1.0113	0.9908	1.0240	1.0099	0.9896
45	1.0276	1.0140	0.9938	1.0266	1.0126	0.9927
50	1.0301	1.0166	0.9967	1.0290	1.0152	0.9955
	$w_1 = 0.9569$ ($x_1 = 0.350$)			$w_1 = 0.9708$ ($x_1 = 0.446$)		
0.1	1.0000	0.9844	0.9610	0.9994	0.9839	0.9606
10	1.0060	0.9911	0.9685	1.0054	0.9904	0.9681
15	1.0089	0.9944	0.9724	1.0084	0.9937	0.9718
20	1.0119	0.9975	0.9758	1.0112	0.9968	0.9753
25	1.0146	1.0005	0.9792	1.0141	0.9998	0.9788
30	1.0173	1.0034	0.9825	1.0168	1.0028	0.9820
35	1.0199	1.0063	0.9857	1.0194	1.0056	0.9852
40	1.0226	1.0090	0.9887	1.0220	1.0084	0.9883
45	1.0250	1.0118	0.9918	1.0246	1.0111	0.9913
50	1.0275	1.0144	0.9947	1.0270	1.0137	0.9942
	$w_1 = 0.9804$ ($x_1 = 0.547$)			$w_1 = 0.9873$ ($x_1 = 0.653$)		
0.1	0.9987	0.9832	0.9602	0.9983	0.9828	0.9599
10	1.0049	0.9900	0.9676	1.0045	0.9897	0.9675
15	1.0080	0.9933	0.9713	1.0075	0.9929	0.9712
20	1.0109	0.9964	0.9749	1.0103	0.9961	0.9748
25	1.0137	0.9994	0.9783	1.0131	0.9991	0.9782
30	1.0164	1.0024	0.9815	1.0158	1.0021	0.9815
35	1.0190	1.0053	0.9847	1.0185	1.0050	0.9847
40	1.0216	1.0080	0.9878	1.0212	1.0078	0.9878
45	1.0242	1.0107	0.9908	1.0237	1.0105	0.9908
50	1.0267	1.0134	0.9937	1.0261	1.0132	0.9937
	$w_1 = 0.9925$ ($x_1 = 0.763$)			$w_1 = 0.9967$ ($x_1 = 0.879$)		
0.1	0.9980	0.9828	0.9598	0.9979	0.9827	0.9598
10	1.0043	0.9895	0.9674	1.0042	0.9895	0.9674
15	1.0071	0.9928	0.9711	1.0071	0.9927	0.9711
20	1.0101	0.9959	0.9747	1.0100	0.9959	0.9746
25	1.0129	0.9989	0.9780	1.0128	0.9989	0.9780
30	1.0156	1.0019	0.9814	1.0156	1.0018	0.9813
35	1.0182	1.0047	0.9846	1.0182	1.0047	0.9845
40	1.0209	1.0075	0.9877	1.0208	1.0075	0.9876
45	1.0234	1.0102	0.9907	1.0234	1.0102	0.9906
50	1.0258	1.0129	0.9936	1.0258	1.0129	0.9935

[a] w_1 = mass fraction of component 1. [b] x_1 = mole fraction of component 1; calculated with molecular weights of 4960 and 120.151 for PPG-4000 and acetophenone, respectively.

and π for PPG + 1-octanol and PPG + acetophenone, respectively. With these tabulated ρ_o, C, and D values, the Tait equation reproduces the densities at pressures higher than 0.1 MPa to within the experimental uncertainty.

Figures 3 and 4 show that all of the $P-V-T$ data are merged onto a single curve, when $(P - 0.1)\kappa_{To}$ is plotted against $(V_o/V) - 1$. The relation can be expressed by the following empirical equation with two characteristic parameters, δ_1 and δ_2

$$\kappa_{To}(P - 0.1) = \delta_1\left(\frac{V_o}{V} - 1\right)^{\delta_2} \tag{4}$$

where κ_{To} and V_o are the isothermal compressibility and the specific volume at 0.1 MPa, respectively. The isothermal compressibility κ_T at any pressure is calculated from its definition with the aid of the Tait equation

$$\kappa_T = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,x} = \frac{V_o}{V}\left(\frac{C}{D + P}\right) \tag{5}$$

Table 4. Density at 0.1 MPa (ρ_o) and Correlated Results of the Tait Equation for PPG-4000 (1) + 1-Octanol (2)

T/K	w_1[a]	x_1[b]	ρ_o/g cm^{-3}	C	D/MPa	$10^5\pi$[c]
298.15	0.0	0.0	0.8216	0.08441	106.70	3.3
	0.7734	0.082	0.9534	0.08308	123.00	1.6
	0.8848	0.168	0.9745	0.08078	121.70	1.4
	0.9294	0.257	0.9830	0.07960	120.10	1.3
	0.9534	0.350	0.9876	0.07726	116.50	1.9
	0.9685	0.446	0.9906	0.07939	121.50	1.2
	0.9788	0.547	0.9928	0.07737	117.40	2.6
	0.9862	0.653	0.9945	0.08437	130.80	1.1
	0.9919	0.763	0.9958	0.07915	121.50	2.4
	0.9964	0.879	0.9969	0.08015	125.17	5.7
	1.0	1.0	0.9979	0.07820	120.30	2.0
318.15	0.0	0.0	0.8077	0.07419	79.68	6.2
	0.7734	0.082	0.9381	0.08188	108.00	1.3
	0.8848	0.168	0.9593	0.09542	131.80	5.4
	0.9294	0.257	0.9680	0.08178	111.30	1.8
	0.9534	0.350	0.9724	0.08356	115.60	6.9
	0.9685	0.446	0.9755	0.07480	100.40	3.3
	0.9788	0.547	0.9776	0.08167	111.50	3.4
	0.9862	0.653	0.9792	0.07359	99.17	5.0
	0.9919	0.763	0.9805	0.08107	112.00	1.5
	0.9964	0.879	0.9817	0.08559	120.17	5.4
	1.0	1.0	0.9828	0.08390	116.90	1.8
348.15	0.0	0.0	0.7855	0.08988	85.48	2.8
	0.7734	0.082	0.9149	0.08625	97.54	2.2
	0.8848	0.168	0.9362	0.08741	100.60	5.5
	0.9294	0.257	0.9451	0.08051	92.93	2.2
	0.9534	0.350	0.9496	0.08246	96.47	1.8
	0.9685	0.446	0.9527	0.08050	93.78	1.6
	0.9788	0.547	0.9547	0.08149	95.48	1.7
	0.9862	0.653	0.9563	0.08041	94.46	1.3
	0.9919	0.763	0.9576	0.08865	106.30	2.0
	0.9964	0.879	0.9589	0.09545	116.89	3.7
	1.0	1.0	0.9600	0.09113	110.70	2.9

[a] w_1 = mass fraction of component 1. [b] x_1 = mole fraction of component 1; calculated with molecular weights of 4960 and 130.231 for PPG-4000 and 1-octanol, respectively. [c] π defined as in eq 3.

Table 5. Density at 0.1 MPa (ρ_o) and Correlated Results of the Tait Equation for PPG-4000 (1) + Acetophenone (2)

T/K	w_1[a]	x_1[b]	ρ_o/g cm^{-3}	C	D/MPa	$10^5\pi$[c]
298.15	0.0	0.0	1.0224	0.09612	169.40	5.4
	0.7872	0.082	1.0052	0.08945	145.30	3.9
	0.8927	0.168	1.0026	0.09486	153.40	6.3
	0.9345	0.257	1.0011	0.08806	137.20	5.8
	0.9569	0.350	1.0000	0.10230	166.10	7.3
	0.9708	0.446	0.9994	0.10020	161.00	5.4
	0.9804	0.547	0.9987	0.09416	148.10	8.1
	0.9873	0.653	0.9983	0.08956	140.60	4.1
	0.9925	0.763	0.9980	0.09059	141.80	8.4
	0.9967	0.879	0.9979	0.08870	138.20	6.2
	1.0	1.0	0.9979	0.07820	120.30	2.0
318.15	0.0	0.0	1.0053	0.08784	137.00	2.8
	0.7872	0.082	0.9892	0.09292	135.30	4.7
	0.8927	0.168	0.9867	0.08972	128.20	4.1
	0.9345	0.257	0.9853	0.09138	130.30	6.6
	0.9569	0.350	0.9844	0.08783	124.30	3.7
	0.9708	0.446	0.9839	0.09951	144.30	6.3
	0.9804	0.547	0.9832	0.09026	127.30	7.9
	0.9873	0.653	0.9828	0.07300	98.65	3.7
	0.9925	0.763	0.9828	0.08480	118.50	2.6
	0.9967	0.879	0.9827	0.08468	118.10	2.4
	1.0	1.0	0.9828	0.08390	116.90	1.8
348.15	0.0	0.0	0.9792	0.08757	114.40	3.1
	0.7872	0.082	0.9651	0.09407	117.90	4.4
	0.8927	0.168	0.9632	0.08517	103.00	2.7
	0.9345	0.257	0.9620	0.08794	106.50	5.2
	0.9569	0.350	0.9610	0.08714	104.90	6.2
	0.9708	0.446	0.9606	0.08671	104.30	3.5
	0.9804	0.547	0.9602	0.08498	102.10	5.6
	0.9873	0.653	0.9599	0.08841	106.00	3.0
	0.9925	0.763	0.9598	0.08868	106.50	3.3
	0.9967	0.879	0.9598	0.08510	101.70	2.7
	1.0	1.0	0.9600	0.09113	110.70	2.9

[a] w_1 = mass fraction of component 1. [b] x_1 = mole fraction of component 1; calculated with molecular weights of 4960 and 120.151 for PPG-4000 and acetophenone, respectively. [c] π defined as in eq 3.

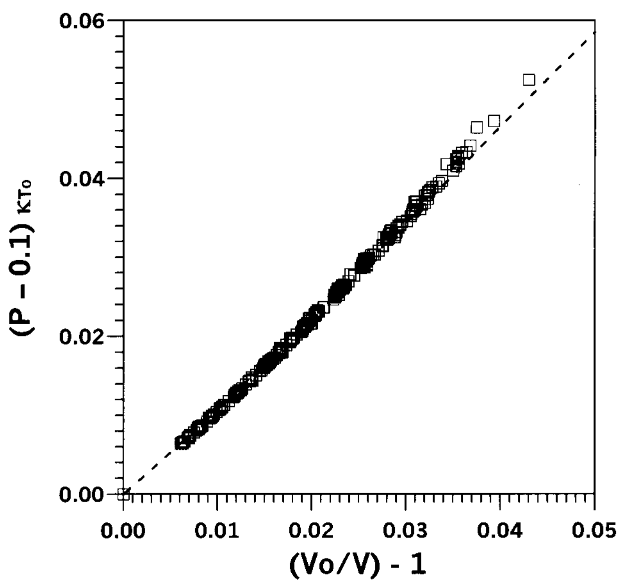

Figure 3. Generalized correlation of the $P-V-T$ data for PPG-4000 (1) + 1-octanol (2) at different compositions.

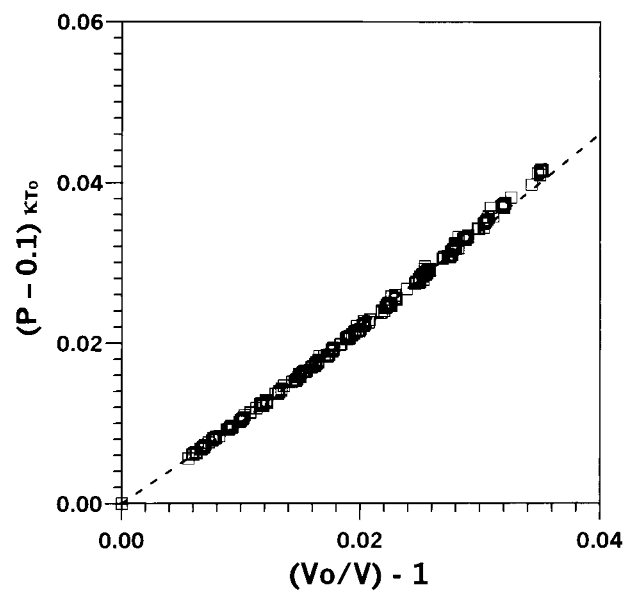

Figure 4. Generalized correlation of the $P-V-T$ data for PPG-4000 (1) + acetophenone (2) at different compositions.

where V is the specific volume and the constants C and D are taken from Tables 4 and 5. The characteristic parameters δ_1 and δ_2 are 1.4000 and 1.0577 for PPG + 1-octanol and 1.4215 and 1.0651 for PPG + acetophenone, respectively. The dashed lines in Figures 3 and 4 are the correlated results. This empirical equation, eq 4, correlates the density ρ to absolute average deviations (AADs) of 0.028 and 0.021% overall, with maximum deviations (at 50 MPa) of 0.23 and 0.15% for PPG + 1-octanol and PPG + acetophenone, respectively. As a consequence, the characteristic parameters δ_1 and δ_2 can be determined from a few experimental data points (in principle, two points will be sufficient) for any given composition. Once the parameters are determined, eq

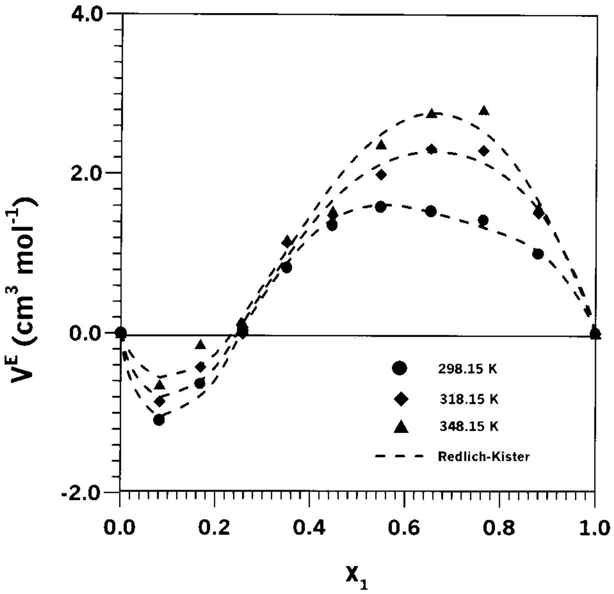

Figure 5. Variations of excess volume with composition for PPG-4000 (1) + 1-octanol (2) at 0.1 MPa.

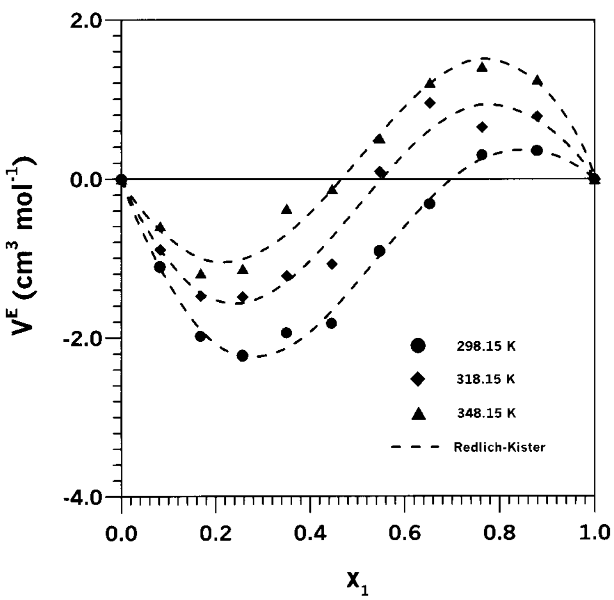

Figure 6. Variations of excess volume with composition for PPG-4000 (1) + acetophenone (2) at 0.1 MPa.

4 can be used to estimate the density at elevated pressures from the density at atmospheric pressure (or other reference pressure), κ_{T0}, and V_0.

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 using

$$V^E = V_m - x_1 V_1^o - x_2 V_2^o \qquad (6)$$

with

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho} \qquad (7)$$

where V_m is the molar volume of the mixture. x_i, V_i^o, 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 variations with composition of the excess volumes at 0.1 MPa are s-shaped, as shown in Figures 5 and 6 for PPG + 1-octanol and PPG + acetophenone, respectively. Negative excess volumes are exhibited in the solvent-rich region, whereas V^E changes to be positive as the mole

Table 6. Correlated Results of the Redlich–Kister Equation for PPG-4000 (1) + 1-Octanol (2) and PPG-4000 (1) + Acetophenone (2)

T/K	P/MPa	A_0	A_1	A_2	A_3	AAD[a]/cm^3 mol^{-1}
		PPG-4000 (1) + 1-Octanol (2)				
298.15	0.1	6.7412	4.4420	−11.4616	13.9606	0.045
	10	7.0081	5.8569	−11.6396	10.3949	0.063
	15	6.4713	5.2216	−10.5825	11.5364	0.094
	20	6.0588	5.7770	−9.6676	10.2031	0.104
	25	6.7231	5.8344	−10.8850	9.6119	0.083
	30	6.3384	5.7437	−10.3363	9.8248	0.054
	35	5.6555	4.5579	−9.1849	11.5125	0.091
	40	5.8045	5.0119	−9.3538	10.9908	0.086
	45	6.0799	4.6494	−9.9308	10.7897	0.102
	50	5.7342	3.8896	−9.3710	12.2057	0.096
318.15	0.1	8.3187	10.2297	−9.8086	4.6550	0.112
	10	6.9592	7.1805	−4.6298	10.2133	0.138
	15	6.4474	4.8023	−4.9910	12.2048	0.223
	20	7.1388	8.6131	−7.9739	3.6591	0.204
	25	7.1604	8.5759	−9.6205	1.7431	0.279
	30	7.3332	8.0564	−9.6984	2.1313	0.273
	35	7.1322	8.1066	−9.2762	1.7837	0.283
	40	6.9264	8.6979	−9.5849	0.3360	0.166
	45	7.0436	7.9839	−10.6238	−0.3627	0.304
	50	6.7838	8.6655	−8.7059	0.1975	0.244
348.15	0.1	8.9758	12.7893	−6.7413	0.9755	0.148
	10	6.6093	11.6780	−10.0255	−6.1114	0.255
	15	6.7239	13.1302	−11.9512	−10.1965	0.301
	20	6.8951	13.2420	−10.6309	−8.6708	0.252
	25	6.8048	13.8992	−10.6107	−9.9818	0.256
	30	6.3832	11.9259	−9.8003	−7.0925	0.228
	35	6.7604	12.2482	−10.3661	−8.1585	0.216
	40	7.2282	13.8949	−11.0901	−11.0277	0.218
	45	7.1005	12.7861	−10.9410	−9.7649	0.195
	50	7.0326	12.4496	−10.7300	−9.4239	0.181
		PPG-4000 (1) + Acetophenone (2)				
298.15	0.1	−4.8431	14.3625	0.8183	−2.6673	0.055
	10	−4.0205	13.5252	−1.2510	−5.1123	0.146
	15	−4.2060	14.3477	−0.8586	−6.0091	0.179
	20	−4.4960	13.9001	−0.5800	−5.6367	0.179
	25	−3.8350	13.9182	−1.8964	−5.5989	0.159
	30	−3.9371	13.6359	−2.7010	−7.7662	0.193
	35	−4.0122	14.0934	−2.7920	−8.4421	0.203
	40	−4.2843	13.5583	−1.9474	−7.8958	0.189
	45	−4.3033	13.4933	−2.1528	−7.5296	0.199
	50	−4.3913	13.8325	−1.8748	−8.4324	0.190
318.15	0.1	−1.5035	13.9576	−0.8800	−3.0996	0.094
	10	−1.4282	12.0225	−0.9408	−0.3229	0.045
	15	−1.7306	11.7005	−0.0662	−0.1591	0.037
	20	−1.4261	11.5825	−2.0156	−2.5644	0.068
	25	−1.2964	11.0737	−0.7310	0.2722	0.045
	30	−1.4807	10.1756	−0.2812	1.6545	0.055
	35	−1.2854	10.7989	−0.2610	0.4234	0.095
	40	−1.3326	10.8508	−2.2631	−1.6345	0.076
	45	−1.1711	10.8766	−0.7417	0.2854	0.095
	50	−1.3091	9.9634	−0.6933	1.4498	0.089
348.15	0.1	1.2415	14.0111	0.3138	−2.2777	0.107
	10	0.4234	12.4298	−2.5851	−5.0262	0.206
	15	−0.1129	14.4181	−1.2147	−8.6178	0.150
	20	0.0768	12.6533	−1.3236	−6.6557	0.191
	25	0.0619	13.4640	−1.1171	−7.8116	0.162
	30	−0.0590	11.1894	−3.3788	−5.9603	0.180
	35	−0.1964	11.5541	−2.7780	−7.2810	0.179
	40	0.2860	11.4748	−1.6439	−5.2146	0.185
	45	0.1591	12.2808	−1.1535	−7.3463	0.198
	50	−0.0862	10.2992	0.5522	−1.2792	0.222

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

Table 7. 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}
PPG-4000	483.7	6227	0.8401	0.00043	498.9	5543	0.8297	0.00032
1-octanol	494.9	5627	0.9947	0.00058	511.1	4945	0.9794	0.00053
acetophenone	627.4	5838	0.8076	0.00027	649.2	5138	0.7954	0.00015

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

fraction of PPG is increased. The excess volumes increase with increasing temperature over the whole composition range. The volume contraction (negative excess volume) is likely a result of the formation of hydrogen bonds between dissimilar components. The effects of hydrogen bonding become smaller with increasing temperature, which is in accordance with the experimental results shown in Figures 5 and 6. The excess volumes are correlated with the Redlich–Kister equation

$$V^{\mathrm{E}} = x_1 x_2 \sum_{k=0}^{3} A_k (x_1 - x_2)^k \qquad (8)$$

Table 6 gives the correlated results. The dashed lines in Figures 5 and 6 are the calculated results from the Redlich–Kister equation.

P–*V*–*T* Data Correlation with Equations of State

P–V–T data for polymers are needed for the development of correlation methods. The experimental specific volumes were correlated with two polymer equations of state (EOSs): the Flory–Orwoll–Vrij (FOV)[25] and the Schotte.[26] These EOS were expressed as follows

FOV EOS

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{\bar{V}^{1/3}}{\bar{V}^{1/3} - 1} - \frac{1}{\bar{T}\bar{V}} \qquad (9)$$

Schotte EOS

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{RT^*}{P^*MV^*}\left(1 - \frac{1}{\bar{V}^{1/3}}\right) + \frac{1}{\bar{V}^{1/3} - 1} - \frac{1}{\bar{T}\bar{V}} \qquad (10)$$

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 P–V–T data. Table 7 lists the calculated results for 1-octanol, acetophenone, and PPG. The tabulated characteristic parameters were further employed to calculate the specific volumes of the polymer solutions via the following mixing rules[26]

$$V_{\mathrm{m}}^* = \left[M_{\mathrm{m}}\left(\frac{\Psi_1}{M_1 V_1^*} + \frac{\Psi_2}{M_2 V_2^*}\right)\right]^{-1} \qquad (11)$$

$$T_{\mathrm{m}}^* = \frac{P_{\mathrm{m}}^*}{\dfrac{\Psi_1 P_1^*}{T_1^*} + \dfrac{\Psi_2 P_2^*}{T_2^*}} \qquad (12)$$

and

$$P_{\mathrm{m}}^* = \Psi_1{}^2 P_1^* + \Psi_2{}^2 P_2^* + 2\Psi_1\Psi_2 P_{12}^* \qquad (13)$$

Table 8. 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]
PPG-4000 + 1-octanol	0.0002	0.061	−0.0004	0.056
PPG-4000 + acetophenone	−0.0430	0.059	−0.0439	0.050

[a] AAD/% = $100/n\sum_{k=1}^{n}|V_{k,\mathrm{calc}} - V_{k,\mathrm{expt}}|V_{k,\mathrm{expt}}$, where n is the number of data points and V is the specific volume.

with

$$\Psi_i = \frac{w_i V_i^*}{w_1 V_1^* + w_2 V_2^*} \qquad (14)$$

and

$$P_{12}^* = (1 - \Delta_{12})(P_1^* P_2^*)^{0.5} \qquad (15)$$

where Ψ_i, M_i, and w_i represent the segment volume fraction, the number-average molecular weight, and the weight fraction, respectively, of component i. Δ_{12} in eq 15 is a binary interaction constant that was determined from the P–V–T data for each binary system. The calculated results are reported in Table 8. Both the FOV and the Schotte EOS represent quantitatively the P–V–T behavior of PPG + 1-octanol and PPG + acetophenone over the entire experimental conditions.

Conclusions

P–V–T properties have been measured for PPG-4000 + 1-octanol and PPG-4000 + acetophnone at temperatures from 298.15 to 348.15 K and pressures up to 50 MPa. The Tait equation accurately represented the effect of pressure on the liquid density for the two investigated systems. Moreover, all of the P–V–T data were also well correlated by a generalized equation with two characteristic parameters. The excess volumes were found to vary from negative to positive with increasing mole fraction of PPG. Both the FOV and the Schotte EOS satisfactorily correlated the P–V–T data for these two polymeric systems.

Acknowledgment. The financial support of the National Science Council, ROC, through Grant NSC89-2214-E011-045 is gratefully acknowledged.

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MA010204F