PVT Measurements for Mixtures of 1-Octanol with Oligomeric Poly(ethylene glycol) from 298 K to 338 K and Pressures up to 30 MPa

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PVT properties were measured for mixtures of 1-octanol with fractionation cuts of poly(ethylene glycol)-200 or poly(ethylene glycol)-600 at temperatures from 298 K to 338 K and pressures up to 30 MPa. Excess volumes are positive for these two polymer solution systems. The pressure effect on the liquid densities was represented accurately by the Tait equation, with which the isothermal compressibilities were calculated. Both the Flory−Orwoll−Vrij and the Schotte equations of state were employed to correlate the experimental specific volumes. Accurate results were obtained from these two equations.

Introduction

Volumetric properties of polymer solutions are needed in polymer processing and also useful for development of polymer equations of state. This study was undertaken to investigate the *PVT* behavior of polymer solutions containing fractionation cuts of oligomeric poly(ethylene glycol) (PEG). Dee et al. (1992) reported the *PVT* properties for various polymer liquids, including polyethylene, poly(dimethylsiloxane), poly(ethylene glycol) (PEG), and poly(propylene glycol) (PPG) in the temperature range room temperature to 250 °C and for pressures up to 200 MPa. Their results were presented graphically together with the determined characteristic parameters of the Flory−Orwoll−Vrij (FOV) equation of state for each polymer liquid. The densities (or specific volumes) of aqueous PEGs and of oligomeric propylene glycols were measured by Muller and Rasmussen (1991) and also by Sandell and Goring (1971) at atmospheric pressure. Earlier *PVT* data of polymers have been extensively compiled by Zoller and Walsh (1995) over wide ranges of temperature and pressure. Recently, Lee et al. (1998) reported the volumetric properties of poly(ethylene glycol methyl ether)-350 (PEGME-350), PEG-200, PEG-600, and blended mixtures of PEGME-350 with PEG-200 or PEG-600 at temperatures from 298.15 K to 338.15 K and pressures up to 30 MPa. In the present study, the *PVT* data were determined for two “binary” systems composed of 1-octanol with PEG-200 or PEG-600 at temperatures from 298.15 K to 338.15 K and pressures up to 30 MPa. These new experimental results complement information on the volumetric behavior of the oligomeric solutions in response to the effects of temperature, pressure, and composition.

Experimental Section

The fractionation cuts of PEG-200 and PEG-600 were purchased from Aldrich Chemical Co. (Milwaukee, WI) with number-average molecular weights (M_n) of approximately 200 and 600, respectively. The apparatus used in the present study is the same as that described by Chang et al. (1995). Liquid mixture samples, prepared by mass to an accuracy of ±0.0001 in mass fraction, were delivered into a high-pressure densimeter (DMA-512, Anton Paar) via a hand pump (model-2426-801, Ruska). The pressure in the measuring cell was manipulated by the hand pump and monitored with a pressure transducer (Model-PDCR 330, 0-40 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 silicon oil 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 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 unit (Anton Paar) and was converted into density (ρ_i) via

$$\rho_{\mathbf{i}} = A(t_i^{\,2} - B) \qquad (1)$$

where A and B are apparatus parameters determined by using the literature *PVT* data of two calibration fluids: pure water (Haar et al., 1984) and dry nitrogen (Vargaftik, 1975). The calibration was made at each temperature of interest over (0.1−30) MPa. Parameter A decreases linearly with increasing both pressure and temperature. The calibration reproduced water densities with an average absolute deviation of 0.01% over the entire range of calibrated conditions. The accuracy of density measurements was estimated to be ±0.0001 g·cm^{-3}.

Results and Discussion

Table 1 compares the densities (ρ) measured from this work with literature values for PEG-600 and 1-octanol. The agreement is in general within ±0.1%. Table 2 lists the experimental densities and the calculated isothermal compressibilities (κ_T) of 1-octanol, while those of PEG-200 and PEG-600 have been reported by Lee et al. (1998). Tables 3

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Table 1. Comparison of Experimental Densities with Literature Values for PEG-600 and 1-Octanol

substance	T/K	P/MPa	ρ/(g·cm^{-3}) this work	ρ/(g·cm^{-3}) lit.	data source
PEG-600	298.15	0.1	1.1212	1.1223	Sandell and Goring (1971)
1-octanol	298.15	0.1	0.8212	0.8211	Rauf and Stewart (1983)
				0.8212	Sastry and Valand (1998)
				0.8218	Wagner and Heintz (1986)
				0.8219	Vijayalakshml and Naidu (1990)
				0.8223	TRC Tables (1993)
				0.8226	Diaz Pena and Tardajos (1979)
1-octanol	328.15	0.1	0.8001	0.8012	Garg et al. (1993)
				0.8007[a]	TRC Tables (1993)
1-octanol	328.15	5.0	0.8039	0.8045	Garg et al. (1993)
1-octanol	328.15	10.0	0.8076	0.8077	Garg et al. (1993)
1-octanol	338.15	0.1	0.7930	0.7934	Garg et al. (1993)
				0.7932[b]	TRC Tables (1993)
1-octanol	338.15	5.0	0.7970	0.7969	Garg et al. (1993)
1-octanol	338.15	10.0	0.8008	0.8002	Garg et al. (1993)

[a] 0.8007 g·cm^{-3} was obtained by the average of 0.8044 (at 323.15 K) and 0.7970 (at 333.15 K). [b] 0.7932 g·cm^{-3} was obtained by the average of 0.7970 (at 333.15 K) and 0.7893 (at 343.15 K).

Table 2. Experimental Density and Calculated Isothermal Compressibility for 1-Octanol

	T/K = 298.15		T/K = 318.15		T/K = 328.15		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}	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}
0.1	0.8212	8.203	0.8073	9.296	0.8001	9.825	0.7930	10.433
5	0.8244	7.833	0.8109	8.847	0.8039	9.322	0.7970	9.847
10	0.8275	7.488	0.8145	8.434	0.8076	8.862	0.8008	9.314
15	0.8306	7.175	0.8178	8.059	0.8110	8.445	0.8044	8.838
20	0.8336	6.889	0.8210	7.717	0.8144	8.069	0.8079	8.411
25	0.8364	6.624	0.8241	7.404	0.8176	7.725	0.8112	8.025
30	0.8391	6.380	0.8271	7.117	0.8206	7.411	0.8144	7.674

and 4 present the results of the experimental ρ and calculated κ_T for PEG-200 + 1-octanol and PEG-600 + 1-octanol, 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):

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

where n is the number of data points. $\rho_{k,\mathrm{calc}}$ and $\rho_{k,\mathrm{expt}}$ represent the calculated and experimental densities for the kth point, respectively. Table 5 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:

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

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 via

$$V^E = V_m - x_1 V_1° - x_2 V_2° \tag{5}$$

with

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho} \tag{6}$$

where V_m is the molar volume of a mixture. x_i, $V_i°$, and M_i are the mole fraction, the molar volume, and the molecular weight, respectively, for component i. The uncertainty of the calculated excess volumes was estimated to be about $\pm$0.05 cm^3·mol^{-1}. Positive excess volumes were obtained for these two polymer solution systems, implying that volume expansion occurs upon blending 1-octanol with these oligomeric substances. It is suggested that the interactions between the hydroxyl group of 1-octanol and the etheric group of PEG are so weak that the heat of mixing could be positive and, thus, the whole mixing process is governed by a positive entropy of mixing. Figure 1 shows the effects of both temperature and pressure on V^E for PEG-600 + 1-octanol. The excess volumes appear to increase with a decrease of temperature and with an increase of pressure. Similar behavior is also found in PEG-200 + 1-octanol. The excess volumes at constant temperature and pressure were correlated with a Redlich−Kister type equation:

$$V^E/x_1x_2 = \sum_{k=1}^{3} E_k (x_1 - x_2)^{k-1} \tag{7}$$

The optimized values of E_k as determined by a least-squares algorithm are tabulated in Table 6, and the calculated results are represented by the dashed curves in Figure 1.

PVT Data Correlation with Equations of State

PVT data of polymers are useful for development of correlation methods needed in polymer processing. The

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

	T/K = 298.15		T/K = 318.15		T/K = 328.15		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}	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}
w_1 = 0.1458[a] (x_1 = 0.100)[b]								
0.1	0.8534	7.840	0.8394	8.533	0.8320	9.131	0.8248	9.650
5	0.8566	7.453	0.8428	8.168	0.8356	8.666	0.8286	9.137
10	0.8597	7.098	0.8462	7.828	0.8392	8.240	0.8323	8.669
15	0.8627	6.776	0.8495	7.516	0.8427	7.857	0.8358	8.248
20	0.8656	6.483	0.8526	7.229	0.8458	7.507	0.8392	7.868
25	0.8683	6.215	0.8556	6.964	0.8489	7.189	0.8425	7.524
30	0.8710	5.969	0.8586	6.720	0.8519	6.898	0.8455	7.208
w_1 = 0.2774 (x_1 = 0.200)								
0.1	0.8849	7.320	0.8707	7.856	0.8630	8.500	0.8558	9.110
5	0.8880	6.970	0.8740	7.585	0.8665	8.094	0.8596	8.617
10	0.8910	6.646	0.8773	7.329	0.8700	7.721	0.8632	8.167
15	0.8939	6.352	0.8805	7.090	0.8732	7.380	0.8666	7.763
20	0.8967	6.084	0.8835	6.866	0.8764	7.071	0.8699	7.399
25	0.8997	5.839	0.8865	6.658	0.8794	6.787	0.8730	7.069
30	0.9020	5.613	0.8894	6.462	0.8824	6.526	0.8760	6.768
w_1 = 0.3969 (x_1 = 0.300)								
0.1	0.9159	6.769	0.9015	7.465	0.8936	7.941	0.8863	8.425
5	0.9189	6.479	0.9047	7.138	0.8970	7.569	0.8899	7.994
10	0.9218	6.208	0.9079	6.834	0.9003	7.225	0.8934	7.598
15	0.9246	5.960	0.9109	6.556	0.9035	6.913	0.8967	7.241
20	0.9273	5.731	0.9138	6.300	0.9066	6.627	0.8998	6.917
25	0.9299	5.520	0.9167	6.065	0.9095	6.365	0.9029	6.623
30	0.9325	5.325	0.9195	5.847	0.9124	6.124	0.9058	6.353
w_1 = 0.5059 (x_1 = 0.400)								
0.1	0.9466	6.399	0.9321	6.859	0.8241	7.350	0.9167	7.869
5	0.9495	6.126	0.9351	6.610	0.8273	7.023	0.9201	7.458
10	0.9523	5.871	0.9382	6.375	0.9305	6.719	0.9235	7.084
15	0.9551	5.638	0.9411	6.157	0.9336	6.442	0.9267	6.746
20	0.9577	5.423	0.9440	5.954	0.9366	6.188	0.9297	6.440
25	0.9603	5.224	0.9468	5.765	0.9394	5.954	0.9327	6.162
30	0.9628	5.040	0.9495	5.588	0.9422	5.737	0.9355	5.907
w_1 = 0.6056 (x_1 = 0.500)								
0.1	0.9765	5.974	0.9617	6.463	0.9537	6.851	0.9462	7.318
5	0.9793	5.724	0.9648	6.234	0.9569	6.563	0.9495	6.959
10	0.9821	5.490	0.9677	6.017	0.9599	6.294	0.9528	6.630
15	0.9847	5.275	0.9705	5.815	0.9629	6.047	0.9558	6.331
20	0.9872	5.077	0.9733	5.626	0.9667	5.820	0.9588	6.059
25	0.9897	4.894	0.9761	5.451	0.9685	5.610	0.9616	5.810
30	0.9921	4.724	0.9786	5.286	0.9712	5.415	0.9644	5.581
w_1 = 0.6973 (x_1 = 0.600)								
0.1	1.0061	5.573	0.9910	6.058	0.9830	6.337	0.9756	6.802
5	1.0088	5.328	0.9929	5.823	0.9860	6.091	0.9788	6.469
10	1.0114	5.100	0.9967	5.602	0.9890	5.860	0.9818	6.161
15	1.0139	4.891	0.9994	5.397	0.9918	5.645	0.9848	5.883
20	1.0164	4.700	1.0021	5.208	0.9945	5.447	0.9876	5.629
25	1.0187	4.523	1.0047	5.032	0.9972	5.263	0.9904	5.398
30	1.0210	4.359	1.0072	4.868	0.9998	5.091	0.9931	5.185
w_1 = 0.7818 (x_1 = 0.700)								
0.1	1.0351	5.232	1.0199	5.582	1.0118	5.944	1.0043	6.257
5	1.0376	4.985	1.0226	5.368	1.0146	5.680	1.0072	5.952
10	1.0402	4.757	1.0253	5.167	1.0175	5.436	1.0102	5.671
15	1.0426	4.549	1.0279	4.981	1.0202	5.211	1.0130	5.471
20	1.0450	4.360	1.0304	4.808	1.0228	5.005	1.0157	5.185
25	1.0472	4.185	1.0329	4.648	1.0254	4.816	1.0184	4.973
30	1.0494	4.025	1.0354	4.498	1.0279	4.641	1.0209	4.778
w_1 = 0.8600 (x_1 = 0.800)								
0.1	1.0634	4.921	1.0480	5.195	1.0399	5.518	1.0322	5.790
5	1.0659	4.683	1.0506	5.009	1.0426	5.295	1.0350	5.522
10	1.0683	4.462	1.0532	4.833	1.0453	5.086	1.0378	5.274
15	1.0706	4.262	1.0557	4.670	1.0480	4.894	1.0405	5.048
20	1.0729	4.080	1.0581	4.517	1.0505	4.716	1.0431	4.841
25	1.0751	3.914	1.0605	4.375	1.0529	4.551	1.0456	4.650
30	1.0772	3.760	1.0629	4.241	1.0553	4.397	1.0481	4.475
w_1 = 0.9325 (x_1 = 0.900)								
0.1	1.0916	4.596	1.0760	4.832	1.0680	5.180	1.0603	5.313
5	1.0940	4.379	1.0785	4.651	1.0706	4.942	1.0630	5.099
10	1.0963	4.178	1.0809	4.480	1.0732	4.721	1.0656	4.898
15	1.0986	3.995	1.0833	4.322	1.0757	4.520	1.0682	4.713
20	1.1007	3.828	1.0856	4.175	1.0781	4.335	1.0707	4.542
25	1.1028	3.674	1.0879	4.038	1.0804	4.166	1.0731	4.383
30	1.1049	3.533	1.0901	3.910	1.0827	4.010	1.0755	4.235

[a] w_1: mass fraction of component 1. [b] x_1: mole fraction of component 1; calculated with the molecular weights of 200 and 130.232 for PEG-200 and 1-octanol, respectively.

Table 4. Experimental Density and Calculated Isothermal Compressibility for PEG-600 (1) + 1-Octanol (2)

	T/K = 298.15		T/K = 318.15		T/K = 328.15		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}	ρ/g·cm^{-3}	$10^4\kappa_T$/MPa^{-1}
				$w_1 = 0.3386^a$ ($x_1 = 0.100$)^b				
0.1	0.9019	7.023	0.8875	7.676	0.8797	8.224	0.8724	8.636
5	0.9049	6.697	0.8907	7.362	0.8832	7.833	0.8760	8.206
10	0.9079	6.396	0.8939	7.069	0.8866	7.472	0.8795	7.811
15	0.9107	6.122	0.8971	6.800	0.8898	7.144	0.8829	7.454
20	0.9135	5.871	0.9001	6.551	0.8929	6.844	0.8861	7.129
25	0.9161	5.640	0.9030	6.320	0.8959	6.570	0.8892	6.833
30	0.9187	5.428	0.9058	6.106	0.8988	6.318	0.8922	6.561
				$w_1 = 0.5353$ ($x_1 = 0.200$)				
0.1	0.9567	6.250	0.9418	6.873	0.9340	7.261	0.9265	7.633
5	0.9596	5.988	0.9449	6.590	0.9372	6.933	0.9299	7.278
10	0.9624	5.742	0.9480	6.326	0.9404	6.629	0.9332	6.950
15	0.9651	5.517	0.9509	6.083	0.9435	6.352	0.9364	6.651
20	0.9677	5.309	0.9537	5.858	0.9464	6.097	0.9394	6.377
25	0.9702	5.116	0.9565	5.651	0.9493	5.864	0.9424	6.126
30	0.9727	4.938	0.9592	5.458	0.9520	5.647	0.9452	5.895
				$w_1 = 0.6638$ ($x_1 = 0.300$)				
0.1	0.9968	5.749	0.9813	6.265	0.9734	6.579	0.9657	7.031
5	0.9995	5.493	0.9843	6.038	0.9764	6.314	0.9690	6.699
10	1.0022	5.254	0.9872	5.823	0.9795	6.067	0.9721	6.391
15	1.0048	5.037	0.9900	5.624	0.9824	5.838	0.9752	6.112
20	1.0073	4.837	0.9928	5.439	0.9852	5.627	0.9781	5.857
25	1.0097	4.653	0.9954	5.265	0.9880	5.432	0.9809	5.622
30	1.0120	4.482	0.9980	5.103	0.9907	5.250	0.9836	5.407
				$w_1 = 0.7544$ ($x_1 = 0.400$)				
0.1	1.0270	5.468	1.0116	5.786	1.0035	6.247	0.9958	6.520
5	1.0297	5.200	1.0144	5.589	1.0065	5.964	0.9989	6.218
10	1.0322	4.953	1.0172	5.403	1.0094	5.701	1.0020	5.953
15	1.0348	4.729	1.0199	5.228	1.0122	5.461	1.0049	5.711
20	1.0372	4.525	1.0226	5.066	1.0150	5.241	1.0080	5.490
25	1.0395	4.338	1.0251	4.913	1.0176	5.039	1.0104	5.282
30	1.0418	4.167	1.0277	4.770	1.0201	4.852	1.0130	5.092
				$w_1 = 0.8217$ ($x_1 = 0.500$)				
0.1	1.0509	5.135	1.0351	5.569	1.0268	5.938	1.0193	6.009
5	1.0534	4.884	1.0378	5.345	1.0297	5.687	1.0222	5.800
10	1.0559	4.652	1.0406	5.135	1.0326	5.453	1.0252	5.604
15	1.0584	4.442	1.0432	4.942	1.0353	5.237	1.0280	5.420
20	1.0607	4.251	1.0457	4.763	1.0380	5.039	1.0308	5.248
25	1.0629	4.076	1.0482	4.597	1.0406	4.856	1.0334	5.087
30	1.0652	3.915	1.0507	4.443	1.0431	4.686	1.0360	4.937
				$w_1 = 0.8736$ ($x_1 = 0.600$)				
0.1	1.0704	4.985	1.0546	5.345	1.0462	5.618	1.0384	5.825
5	1.0729	4.727	1.0573	5.107	1.0490	5.381	1.0413	5.599
10	1.0753	4.490	1.0599	4.885	1.0518	5.160	1.0442	5.387
15	1.0777	4.276	1.0624	4.682	1.0544	4.956	1.0470	5.191
20	1.0800	4.082	1.0649	4.496	1.0570	4.769	1.0496	5.008
25	1.0822	3.906	1.0673	4.324	1.0595	4.596	1.0522	4.839
30	1.0843	3.744	1.0696	4.166	1.0619	4.435	1.0547	4.681
				$w_1 = 0.9146$ ($x_1 = 0.699$)				
0.1	1.0861	4.708	1.0702	5.086	1.0617	5.334	1.0539	5.511
5	1.0885	4.491	1.0728	4.903	1.0644	5.133	1.0567	5.337
10	1.0909	4.290	1.0754	4.729	1.0671	4.945	1.0595	5.170
15	1.0932	4.106	1.0779	4.568	1.0697	4.770	1.0622	5.014
20	1.0954	3.938	1.0803	4.418	1.0723	4.608	1.0648	4.868
25	1.0976	3.784	1.0827	4.278	1.0746	4.456	1.0674	4.730
30	1.0997	3.641	1.0850	4.147	1.0771	4.315	1.0698	4.600
				$w_1 = 0.9485$ ($x_1 = 0.800$)				
0.1	1.0999	4.595	1.0838	4.854	1.0752	5.293	1.0673	5.383
5	1.1023	4.380	1.0863	4.657	1.0779	5.059	1.0701	5.193
10	1.1046	4.181	1.0888	4.472	1.0806	4.842	1.0728	5.013
15	1.1069	4.001	1.0912	4.302	1.0832	4.643	1.0755	4.846
20	1.1091	3.835	1.0936	4.145	1.0856	4.460	1.0781	4.690
25	1.1112	3.683	1.0960	4.000	1.0880	4.291	1.0805	4.543
30	1.1133	3.543	1.0973	3.863	1.0904	4.136	1.0829	4.407
				$w_1 = 0.9765$ ($x_1 = 0.900$)				
0.1	1.1113	4.393	1.0949	4.708	1.0865	5.151	1.0786	5.197
5	1.1136	4.217	1.0974	4.581	1.0892	4.924	1.0813	5.033
10	1.1159	4.052	1.0999	4.458	1.0918	4.714	1.0840	4.876
15	1.1181	3.900	1.1023	4.342	1.0943	4.520	1.0866	4.730
20	1.1203	3.759	1.1045	4.231	1.0967	4.343	1.0891	4.592
25	1.1224	3.629	1.1070	4.127	1.0991	4.180	1.0916	4.462
30	1.1244	3.507	1.1092	4.028	1.1014	4.028	1.0940	4.340

[a] w_1: mass fraction of component 1. [b] x_1: mole fraction of component 1; calculated with the molecular weights of 600 and 130.232 for PEG-600 and 1-octanol, respectively.

Table 5. Results of Density Correlation with the Tait Equation

	PEG-200 (1) + 1-octanol (2)			PEG-600 (1) + 1-octanol (2)		
x_1	C	D/MPa	$10^2\pi^a$	C	D/MPa	$10^2\pi^a$
			T/K = 298.15			
0.0	0.07817	95.2	0.005	0.07817	95.2	0.005
0.100	0.06885	87.7	0.002	0.06607	94.0	0.003
0.200	0.06646	90.7	0.002	0.06513	104.1	0.002
0.300	0.06877	101.5	0.003	0.05678	98.8	0.005
0.400	0.06567	102.5	0.002	0.04937	90.2	0.003
0.500	0.06274	104.9	0.002	0.04661	90.7	0.006
0.600	0.05606	100.5	0.004	0.04270	85.6	0.005
0.700[b]	0.04923	94.0	0.004	0.04553	96.6	0.005
0.800	0.04517	91.7	0.003	0.04393	95.5	0.004
0.900	0.04338	94.3	0.003	0.04912	111.7	0.003
			T/K = 318.15			
0.0	0.08216	88.3	0.003	0.08216	88.3	0.003
0.100	0.08536	99.9	0.003	0.08111	105.6	0.003
0.200	0.09713	123.5	0.002	0.07276	105.8	0.003
0.300	0.07386	98.8	0.004	0.07563	121.1	0.002
0.400	0.08189	119.3	0.004	0.07443	128.5	0.004
0.500	0.07911	122.3	0.005	0.06112	109.7	0.004
0.600	0.06844	112.9	0.003	0.05303	99.1	0.004
0.700[b]	0.06424	115.0	0.005	0.06248	122.8	0.002
0.800	0.06411	123.3	0.003	0.05324	109.6	0.007
0.900	0.05733	118.6	0.004	0.07640	162.2	0.004
			T/K = 328.15			
0.0	0.08164	83.0	0.005	0.08146	83.0	0.005
0.100	0.07682	84.0	0.004	0.07454	90.5	0.002
0.200	0.07661	90.0	0.003	0.06991	96.2	0.003
0.300	0.07330	92.2	0.002	0.07143	108.5	0.005
0.400	0.07179	97.6	0.004	0.06049	96.7	0.003
0.500	0.07102	103.6	0.003	0.06176	103.9	0.002
0.600	0.07124	112.3	0.002	0.05887	104.5	0.002
0.700[b]	0.05898	99.1	0.005	0.06276	117.6	0.004
0.800	0.06033	109.2	0.003	0.05311	100.2	0.003
0.900	0.05003	96.5	0.003	0.05201	100.9	0.003
			T/K = 338.15			
0.0	0.07872	75.4	0.002	0.07872	75.4	0.002
0.100	0.07747	80.2	0.003	0.07459	86.3	0.001
0.200	0.07208	79.0	0.005	0.07109	93.0	0.002
0.300	0.07088	84.0	0.004	0.06478	92.0	0.002
0.400	0.06547	83.1	0.002	0.06504	99.9	0.007
0.500	0.06506	88.8	0.003	0.07577	126.0	0.002
0.600	0.06064	89.1	0.005	0.0660	113.2	0.002
0.700[b]	0.05649	90.2	0.007	0.07627	138.3	0.002
0.800	0.05520	95.2	0.005	0.06723	124.8	0.003
0.900	0.05832	109.7	0.003	0.07245	139.3	0.001

[a] π = defined as in eq 3. [b] x_1 = 0.699 for PEG-600 + 1-octanol.

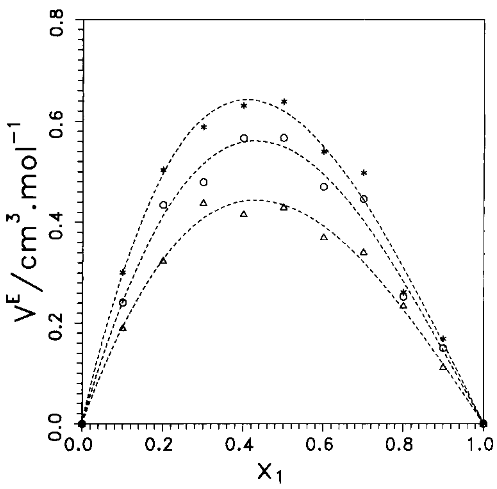

Figure 1. Variations of excess volume with composition for PEG-600 (1) + 1-octanol (2) at 298.15 K and 0.1 MPa (○); 338.15 K and 0.1 MPa (△); 298.15 K and 30 MPa (∗); Redlich−Kister equation (- - -).

specific volumes obtained in the present work were correlated by two polymer equations of state (EOSs): the Flory−Orwoll−Vrij (FOV) equation (1964) and the Schotte equation (1982). These EOSs were expressed as follows.

The FOV EOS:

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{\bar{V}^{1/3}}{\bar{V}^{1/3} - 1} - \frac{1}{\bar{T}\bar{V}} \tag{8}$$

The Schotte EOS:

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{RT^*}{P^*MV^*}\left(1 - \frac{1}{\bar{V}^{1/3}}\right) + \frac{1}{\bar{V}^{1/3} - 1} - \frac{2}{\bar{T}\bar{V}} \tag{9}$$

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 7 lists the calculated results for PEG-200, PEG-600, and 1-octanol. These tabulated values of characteristic properties were also employed to calculate the specific volumes of the polymer solutions via the following mixing rules (Schotte, 1982):

$$V_m^* = \left[M_m\left(\frac{\Psi_1}{M_1 V_1^*} + \frac{\Psi_2}{M_2 V_2^*}\right)\right]^{-1} \tag{10}$$

$$T_m^* = \frac{P_m^*}{\dfrac{\Psi_1 P_1^*}{T_1^*} + \dfrac{\Psi_2 P_2^*}{T_2^*}} \tag{11}$$

Table 6. Results of Excess Volume Correlation with the Redlich–Kister Equation

	PEG-200 (1)+1-octanol (2)				PEG-600 (1)+1-octanol (2)			
P/MPa	E_1	E_2	E_3	10^2AAD[a]	E_1	E_2	E_3	10^2AAD[a]
				T/K = 298.15				
0.1	2.010	0.294	0.880	2.0	2.198	−0.678	−0.056	2.1
5.0	2.007	0.237	0.578	1.7	2.157	−0.862	−0.168	2.4
10.0	2.036	0.359	0.615	2.1	2.279	−0.741	−0.227	2.1
15.0	2.097	0.291	0.514	1.8	2.265	−0.834	0.202	2.2
20.0	2.120	0.233	0.545	2.0	2.376	−1.018	−0.052	2.6
25.0	2.130	0.222	0.599	1.6	2.435	−0.984	0.123	3.0
30.0	2.128	0.215	0.433	1.6	2.479	−0.970	0.128	2.0
				T/K = 318.15				
0.1	1.771	0.221	0.515	1.7	1.914	−0.490	0.167	3.8
5.0	1.856	0.144	0.681	1.4	1.936	−0.693	0.186	3.1
10.0	1.956	0.142	0.909	1.3	2.092	−0.776	0.558	2.5
15.0	2.037	0.227	0.725	1.6	2.163	−0.853	0.207	2.3
20.0	2.076	0.282	0.913	1.7	2.220	−0.470	1.067	4.2
25.0	2.071	0.280	1.006	1.6	2.447	−0.717	0.447	2.2
30.0	2.097	0.309	0.859	1.9	2.512	−0.386	0.950	4.5
				T/K = 328.15				
0.1	2.059	0.211	0.469	2.2	1.853	−0.660	−0.127	2.3
5.0	2.159	0.170	0.617	1.9	2.061	−0.912	−0.324	2.7
10.0	2.232	0.117	0.480	2.0	2.170	−0.973	−0.082	2.4
15.0	2.284	0.240	0.228	2.7	2.278	−0.952	−0.053	2.5
20.0	2.324	0.120	0.534	1.6	2.307	−1.017	0.409	1.9
25.0	2.366	0.156	0.714	1.8	2.392	−1.119	0.177	2.7
30.0	2.344	0.239	0.657	1.8	2.420	−1.124	0.210	1.8
				T/K = 338.15				
0.1	1.874	−0.022	0.229	2.3	1.740	−0.522	−0.010	1.3
5.0	1.967	−0.001	0.370	1.9	1.922	−0.608	0.258	1.5
10.0	2.004	0.108	0.568	1.8	1.962	−0.833	0.306	1.9
15.0	2.046	0.052	0.489	1.9	2.073	−0.808	0.358	1.8
20.0	2.144	0.053	0.453	1.8	2.099	−0.879	0.781	2.8
25.0	2.167	0.112	0.396	2.4	2.289	−1.036	0.399	1.6
30.0	2.187	−0.068	0.471	1.8	2.374	−1.231	0.207	2.0

[a] ADD/(cm^3·mol^{-1}) = $1/n\sum_{i=1}^{n} |V^E_{i,\text{calc}} - V^E_{i,\text{expt}}|$, where n is the number of data points.

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}
1-octanol	456.0	5775	1.0026	0.000 23	471.7	5079	0.9873	0.000 16
PEG-200	738.2	6541	0.7566	0.000 21	783.3	5728	0.7444	0.000 07
PEG-600	752.4	7549	0.7524	0.000 20	813.4	5490	0.7363	0.000 30

[a] AAD = $1/n\sum_{k=1}^{n} |V^E_{k,\text{calc}} - V^E_{k,\text{expt}}|$.

and

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

with

$$\Psi_i = \frac{w_i V_i^*}{w_1 V_1^* + w_2 V_2^*} \qquad (13)$$

and

$$P_{12}^* = (1 - \Delta_{12})(P_1^* P_2^*)^{0.5} \qquad (14)$$

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 14 is a binary interaction constant that was determined from the *PVT* data for each binary system. The calculated results are reported in Table 8. Both the FOV and the Schotte EOSs represent quantitatively the *PVT* behavior of PEG-200 + 1-octanol and PEG-600 + 1-octanol with reasonable accuracy over the entire experimental conditions.

Conclusions

PVT data have been measured for PEG-200 + 1-octanol and PEG-600 + 1-octanol at temperatures from 298 K to 338 K and pressures up to 30 MPa. Volume expansion (positive excess volume) was found upon mixing 1-octanol with PEG-200 and PEG-600. 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 EOSs correlated well the *PVT* data of the polymer solutions.

Table 8. Results of Specific Volume Correlation with the Equations of State for Polymer Blends

	FOV EOS		Schotte EOS	
mixture (1) + (2)	Δ_{12}	AAD%[a]	Δ_{12}	AAD%[a]
PEG-200 + 1-octanol	0.0251	0.04	0.0208	0.04
PEG-600 + 1-octanol	0.0094	0.03	−0.0032	0.04

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

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