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Pressure−Volume−Temperature Properties for Binary Oligomeric Solutions of Poly(ethylene glycol) and Poly(ethylene glycol methyl ether) with Acetophenone up to 50 MPa

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Pressure−volume−temperature (*PVT*) properties were measured with a high-pressure densitometer for the oligomeric solutions of acetophenone + poly(ethylene glycol)-200 (PEG-200) and acetophenone + poly(ethylene glycol methyl ether)-350 (PEGME-350) at temperatures from 298.15 K to 348.15 K and pressures up to 50 MPa. While the excess volumes are positive in acetophenone + PEG-200 over the entire composition range, those are found to change from positive to negative with increasing the mole fraction of the solvent in acetophenone + PEGME-350. The pressure effect on the liquid densities can be represented accurately by the Tait equation. Moreover, an empirical equation with two characteristic parameters correlates well the *PVT* data over the entire experimental conditions for each binary system. The experimental specific volumes were also correlated with the Flory−Orwoll−Vrij (FOV) and the Schotte equations of state to within the experimental uncertainty.

Introduction

Pressure−volume−temperature (*PVT*) properties of polymeric mixtures can form a basis for determining model parameters of equations of state (EOS) and testing the applicability of the EOS with their mixing rules to the polymeric systems. The thermodynamic models with these determined parameters may be further applied to calculate various thermodynamic properties of the mixtures at the conditions of interest for engineering applications. These *PVT* properties may also provide useful supporting evidence to reveal the molecular interactions between the constituent components. As a consequence, *PVT* properties of polymeric systems are fundamentally important for the development of theoretical models and for industrial applications.

The literature *PVT* data of polymeric systems, especially for the mixtures containing oligomeric materials, are relatively scarce in comparison to those of conventional organic mixtures. In addition to Danner and High,[1] Zoller and Walsh[2] tabulated *PVT* data for a variety of polymeric materials and some of polymer solutions and polymer blends. Sandell and Goring[3] and Muller and Rasmussen[4] measured the densities of aqueous oligomeric propylene glycols and aqueous PEG mixtures, respectively. To study the specific interactions between polymers and solvents, Compostizo and co-workers[5−8] have measured the volumetric data for various polymer solutions and blends: poly(4-hydroxystyrene) + acetone, poly(4-hydroxystyrene) + tetrahydrofuran, poly(4-hydroxystyrene) + ethanol, poly(propylene glycol) (PPG) + *n*-hexane, PPG + ethanol, and PEG + PPG. Other sources of *PVT* properties for polymeric mixtures are poly(phenyl oxide) + polystyrene,[9] polystyrene + poly(vinyl methyl ether),[10] poly(vinyl fluoride) + hexafluoropropylene,[11] and polystyrene + tetramethyl bisphenol A polycarbonate.[12] In the recent years, our research group has published *PVT* data of polymeric systems,[13−19] especially for the mixtures containing fractionation cuts of oligomeric PEG, PPG, and PEGME. In the present study, the *PVT* properties were measured for acetophenone + PEG-200 and acetophenone + PEGME-350 at temperatures ranging from 298.15 K to 348.15 K and pressures up to 50 MPa. The experimental results illustrate the volumetric behavior for the oligomeric solutions in response to the effects of temperature, pressure, and composition. These new *PVT* data are correlated with two representative polymeric EOS, the FOV[20] and the Schotte,[21] and the validity of these two EOS is then compared.

Experimental Section

Acetophenone ($w = 0.99$) and the fractionation cuts of PEG-200 and PEGME-350 were purchased from Aldrich Chemical Co. (St. Louis, MO). The number-average molecular weights (M_n) and the poly-dispersities (M_w/M_n) of the oligomeric cuts were measured with a matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF). The values are approximately 260 and 1.0742 for PEG-200 and 366 and 1.0188 for PEGME-350. Each substance has been degassed before use. The schematic diagram of the *PVT* measurement apparatus was presented in Lee et al.[16] The liquid mixture sample was prepared from the degassed compounds by mass to an uncertainty of ± 0.0001 in mass fraction. A high-pressure densitometer (DMA 512 P, Anton Paar, Austria) was used in the density measurements. Pressure in the measuring cell was manipulated by a hand pump and monitored by a pressure transducer (model PDCR 911, 0-70 MPa, Druck, UK) with a digital indicator (model DPI 261, Druck, UK). Pressure measurements were accurate to ± 0.1 % at pressures higher than atmospheric. A thermostatic bath with circulating water regulated the temperature of the measuring cell to within ± 0.03 K. A precision digital thermometer (model 1560, Hart Scientific, USA) incorporated with a thermistor probe measured the bath temperature to an uncertainty of ± 0.02 K. The oscillation period (t_i) of sample i in the vibrating U tube

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Table 1. *PVT* Properties of PEG-200

	$T = 298.15$ K		$T = 318.15$ K		$T = 348.15$ K	
P	ρ	$10^4\ \kappa_T$	ρ	$10^4\ \kappa_T$	ρ	$10^4\ \kappa_T$
MPa	$g\cdot cm^{-3}$	MPa^{-1}	$g\cdot cm^{-3}$	MPa^{-1}	$g\cdot cm^{-3}$	MPa^{-1}
0.1	1.1200	3.9615	1.1038	4.5964	1.0802	5.0593
10	1.1243	3.7519	1.1087	4.3513	1.0854	4.7532
15	1.1264	3.6545	1.1110	4.2373	1.0880	4.6131
20	1.1284	3.5621	1.1134	4.1299	1.0905	4.4813
25	1.1303	3.4742	1.1157	4.0279	1.0929	4.3569
30	1.1323	3.3912	1.1179	3.9308	1.0952	4.2394
35	1.1342	3.3120	1.1201	3.8387	1.0975	4.1285
40	1.1361	3.2367	1.1222	3.7508	1.0998	4.0237
45	1.1379	3.1646	1.1243	3.6671	1.1019	3.9237
50	1.1397	3.0960	1.1263	3.5871	1.1041	3.8293

was displayed with a densitometer of DMA 48 (Anton Paar, Austria), 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 using the literature density data of two calibration fluids: pure water[22] and dry nitrogen.[23] The calibration was made at each measuring temperature over pressures from 0.1 MPa to 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 decrease the accuracy of density measurement by an oscillating densitometer,[24] but the effect is generally minor. The uncertainty of the density measurements, without the correction of viscosity effect, is estimated to within $\pm 5.0 \times 10^{-5}$ $g\cdot cm^{-3}$.

Results and Discussion

The density measurements were conducted in this study at 298.15 K, 318.15 K, and 348.15 K over pressures ranging from 0.1 MPa to 50 MPa. While the densities of acetophenone and PEGME-350 have been reported in Lin et al.[17] and Lee et al.,[18] respectively, the experimental results of PEG-200 are listed in Table 1. The densities of PEG-200 determined from this work agree with those of Lee et al.[13] to within 0.0002 $g\cdot cm^{-3}$ at 298.15 K and 318.15 K under pressures up to 30 MPa. Tables 2 and 3 report the *PVT* properties of the binary systems of acetophenone + PEG-200 and acetophenone + PEGME-350, respectively. The Tait equation was often adopted to represent the pressure dependence of isothermal densities at a given composition. Its expression is given as

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

where ρ_o is density at 0.1 MPa. The optimal values of C and D were determined by fitting the density data to the Tait equation with the following objective function (σ_1):

$$\sigma_1 = \sqrt{\sum_{k=1}^{n}(\rho_{k,\mathrm{calc}} - \rho_{k,\mathrm{expt}})^2/(n-2)} \tag{3}$$

where n is the number of data points; $\rho_{k,\mathrm{calc}}$ and $\rho_{k,\mathrm{expt}}$ stand for the calculated and the experimental densities of the kth point, respectively. Table 4 reports the calculated results. Figure 1 illustrates the densities of acetophenone + PEGME-350 varying with composition at 318.15 K under different pressures. The dashed curves on the graph are the calculated results from the Tait equation, indicating that the agreement between calculated and experimental values is satisfactory.

The isothermal compressibility κ_T at given temperature, pressure, and composition can be calculated from its definition incorporating with the Tait equation and its constants:

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

where V_o is the corresponding specific volume at 0.1 MPa. The calculated isothermal compressibilities are also given in Tables 1 to 3. Figure 2 shows that the isothermal compressibility decreases with an increase of pressure and increases with an increase of temperature.

Assuming that the isothermal bulk modulus linearly depended on pressure, Sanchez et al.[25] developed a generalized equation to represent the *PVT* properties of polymers, solvents, and their solutions. Lin et al.[17] found that the *PVT* data of polymer solutions could also be merged onto a single curve of $(P - 0.1)\ \kappa_{To}$ vs $(V_o/V) - 1$ over the entire experimental range. It was expressed by an empirical equation with two characteristic parameters, δ_1 and δ_2:

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

where κ_{To} and V_o are the isothermal compressibility and the specific volume at 0.1 MPa, respectively. In the data reduction, κ_{To} at given temperature and composition were calculated from eq 4; that is

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

and the Tait constants C and D were taken from Table 4. The empirical model, eq 5, correlates density (ρ) data to an absolute average deviation (AAD) of 0.011 % for acetophenone + PEG-200 (with $\delta_1 = 1.4695$ and $\delta_2 = 1.0725$) and also 0.011 % for acetophenone + PEGME-350 (with $\delta_1 = 1.5115$ and $\delta_2 = 1.0793$). The characteristic parameters δ_1 and δ_2 could be determined from few points of experimental *PVT* data at any given composition. Once the parameters are obtained, eq 5 can be applied to estimate the specific volume at elevated pressures from the knowledge at atmospheric pressure, κ_{To} and V_o.

Furthermore, the excess volume (V^E) or volume change of mixing can be readily calculated from the experimental *PVT* data of liquid mixtures accompanying with those of the constituent compounds via

$$V^E = V_m - (x_1 V_1^o + x_2 V_2^o) \tag{7}$$

with

$$V_m = (x_1 M_1 + x_2 M_2)/\rho \tag{8}$$

where V_m is the molar volume of a mixture; x_i, V_i^o, and M_i are the mole fraction, molar volume, and molecular weight for component i, respectively. The uncertainty of the calculated excess volumes was estimated to be within ± 0.02 $cm^3\cdot mol^{-1}$. Figure 3 depicts the variation of the excess volumes with composition for acetophenone + PEG-200 at 318.15 K. The excess volumes are positive (volume expansion after mixing) over the entire experimental conditions. Figure 4 shows that the excess volumes change from positive to negative as increasing the mole fraction of the solvent in acetophenone + PEGME-350 at 318.15 K. It was suggested that the physical interactions are dominant

Table 2. *PVT* Properties of Acetophenone (1) + PEG-200 (2)

	$T = 298.15$ K		$T = 318.15$ K		$T = 348.15$ K			$T = 298.15$ K		$T = 318.15$ K		$T = 348.15$ K	
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}	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}
$w_1{}^a = 0.0487$ ($x_1{}^b = 0.1000$)													
0.1	1.1146	4.9237	1.0984	5.7498	1.0747	6.5350	30	1.1275	4.3253	1.1124	4.7042	1.0902	5.3867
10	1.1190	4.7069	1.1033	5.3543	1.0800	6.1013	35	1.1292	4.2396	1.1145	4.5668	1.0926	5.2342
15	1.1211	4.6051	1.1057	5.1748	1.0827	5.9045	40	1.1313	4.1576	1.1164	4.4375	1.0949	5.0910
20	1.1233	4.5076	1.1079	5.0072	1.0853	5.7210	45	1.1333	4.0788	1.1187	4.3154	1.0972	4.9558
25	1.1255	4.4143	1.1101	4.8512	1.0878	5.5483	50	1.1352	4.0034	1.1204	4.2004	1.0995	4.8271
$w_1 = 0.1045$ ($x_1 = 0.2000$)													
0.1	1.1086	5.2460	1.0925	5.9285	1.0683	6.8160	30	1.1214	4.4436	1.1064	4.8015	1.0840	5.6125
10	1.1130	4.9487	1.0973	5.4990	1.0738	6.3611	35	1.1235	4.3336	1.1086	4.6550	1.0864	5.4528
15	1.1151	4.8115	1.0996	5.3055	1.0764	6.1549	40	1.1254	4.2291	1.1107	4.5177	1.0888	5.3030
20	1.1173	4.6819	1.1020	5.1257	1.0790	5.9623	45	1.1274	4.1299	1.1128	4.3883	1.0911	5.1615
25	1.1194	4.5593	1.1042	4.9584	1.0815	5.7816	50	1.1294	4.0356	1.1149	4.2666	1.0934	5.0274
$w_1 = 0.1653$ ($x_1 = 0.3000$)													
0.1	1.1024	5.3490	1.0861	6.1097	1.0616	7.1252	30	1.1155	4.6664	1.1003	4.9437	1.0777	5.7472
10	1.1069	5.1005	1.0910	5.6651	1.0673	6.5970	35	1.1175	4.5697	1.1025	4.7923	1.0802	5.5690
15	1.1091	4.9843	1.0934	5.4648	1.0700	6.3609	40	1.1196	4.4770	1.1047	4.6505	1.0825	5.4025
20	1.1113	4.8733	1.0958	5.2788	1.0726	6.1418	45	1.1216	4.3884	1.1068	4.5167	1.0849	5.2455
25	1.1134	4.7673	1.0981	5.1059	1.0752	5.9376	50	1.1235	4.3033	1.1089	4.3912	1.0873	5.0982
$w_1 = 0.2355$ ($x_1 = 0.4000$)													
0.1	1.0953	5.4019	1.0789	6.1638	1.0541	7.1712	30	1.1087	4.6291	1.0935	4.9766	1.0706	5.7969
10	1.0999	5.1170	1.0840	5.7104	1.0599	6.6456	35	1.1108	4.5217	1.0958	4.8229	1.0730	5.6185
15	1.1022	4.9853	1.0865	5.5065	1.0626	6.4098	40	1.1128	4.4194	1.0980	4.6790	1.0755	5.4520
20	1.1043	4.8603	1.0888	5.3173	1.0653	6.1912	45	1.1149	4.3220	1.1002	4.5432	1.0779	5.2950
25	1.1066	4.7414	1.0912	5.1414	1.0679	5.9870	50	1.1169	4.2292	1.1023	4.4161	1.0803	5.1470
$w_1 = 0.3161$ ($x_1 = 0.5000$)													
0.1	1.0871	5.5309	1.0706	6.3400	1.0457	7.4198	30	1.1009	4.7392	1.0855	5.1677	1.0626	5.9175
10	1.0919	5.2395	1.0759	5.8945	1.0516	6.8405	35	1.1031	4.6291	1.0879	5.0146	1.0652	5.7255
15	1.0942	5.1046	1.0783	5.6937	1.0544	6.5825	40	1.1052	4.5248	1.0901	4.8707	1.0677	5.5469
20	1.0965	4.9764	1.0808	5.5061	1.0573	6.3442	45	1.1072	4.4254	1.0924	4.7345	1.0702	5.3792
25	1.0987	4.8545	1.0832	5.3317	1.0599	6.1228	50	1.1093	4.3304	1.0945	4.6064	1.0727	5.2216
$w_1 = 0.4094$ ($x_1 = 0.6000$)													
0.1	1.0779	5.6685	1.0612	6.5619	1.0358	7.5951	30	1.0920	4.8596	1.0766	5.2896	1.0532	6.0932
10	1.0827	5.3704	1.0665	6.0748	1.0419	7.0180	35	1.0941	4.7477	1.0789	5.1253	1.0557	5.8999
15	1.0851	5.2324	1.0692	5.8568	1.0447	6.7599	40	1.0962	4.6404	1.0812	4.9713	1.0583	5.7201
20	1.0874	5.1020	1.0717	5.6541	1.0477	6.5213	45	1.0984	4.5385	1.0836	4.8259	1.0609	5.5509
25	1.0897	4.9774	1.0741	5.4656	1.0504	6.2993	50	1.1004	4.4410	1.0858	4.6901	1.0634	5.3917
$w_1 = 0.5189$ ($x_1 = 0.7000$)													
0.1	1.0674	5.8524	1.0505	6.6829	1.0247	7.7144	30	1.0819	4.9060	1.0663	5.3565	1.0428	6.1432
10	1.0724	5.4988	1.0560	6.1734	1.0310	7.1079	35	1.0842	4.7779	1.0687	5.1862	1.0455	5.9430
15	1.0749	5.3369	1.0587	5.9458	1.0341	6.8380	40	1.0863	4.6565	1.0712	5.0271	1.0482	5.7566
20	1.0772	5.1847	1.0613	5.7346	1.0371	6.5891	45	1.0886	4.5419	1.0735	4.8771	1.0508	5.5818
25	1.0796	5.0411	1.0638	5.5389	1.0399	6.3575	50	1.0907	4.4324	1.0758	4.7369	1.0533	5.4176
$w_1 = 0.6490$ ($x_1 = 0.8000$)													
0.1	1.0548	6.0437	1.0378	6.7131	1.0118	7.9190	30	1.0698	4.9808	1.0542	5.4581	1.0305	6.2936
10	1.0600	5.6425	1.0436	6.2352	1.0183	7.2907	35	1.0721	4.8401	1.0567	5.2946	1.0333	6.0869
15	1.0625	5.4605	1.0463	6.0203	1.0215	7.0117	40	1.0743	4.7070	1.0592	5.1412	1.0360	5.8949
20	1.0650	5.2902	1.0490	5.8199	1.0246	6.7539	45	1.0766	4.5818	1.0616	4.9960	1.0387	5.7145
25	1.0674	5.1306	1.0516	5.6330	1.0276	6.5151	50	1.0788	4.4634	1.0639	4.8596	1.0414	5.5453
$w_1 = 0.8060$ ($x_1 = 0.9000$)													
0.1	1.0401	6.1923	1.0229	6.9269	0.9968	8.1436	30	1.0556	5.0963	1.0399	5.5851	1.0162	6.3891
10	1.0456	5.7779	1.0287	6.4130	1.0036	7.4600	35	1.0581	4.9515	1.0425	5.4120	1.0192	6.1691
15	1.0482	5.5904	1.0317	6.1833	1.0069	7.1582	40	1.0604	4.8143	1.0450	5.2499	1.0220	5.9657
20	1.0508	5.4149	1.0344	5.9695	1.0101	6.8810	45	1.0627	4.6854	1.0475	5.0967	1.0248	5.7750
25	1.0532	5.2503	1.0372	5.7707	1.0132	6.6251	50	1.0650	4.5635	1.0499	4.9533	1.0275	5.5966

[a] w_1, mass fraction of component 1. [b] x_1, mole fraction of component 1, calculated with the molecular weights of 120.151 and 260.0 for acetophenone and PEG-200, respectively.

in the PEGME-350-rich region, leading to volume expansion, whereas the chemical interactions are dominant in the acetophenone-rich region, resulting in volume contraction. The excess volumes at constant temperature and pressure were correlated with a Redlich−Kister type equation:

$$V^E/x_1x_2 = \sum_{k=0}^{2} E_k(x_1 - x_2)^k \tag{9}$$

The optimial values of E_k as determined by a least-squares algorithm are listed in Table 5, in which the root-mean-square deviation (σ_2) is defined as:

$$\sigma_2 = \sqrt{\sum_{k=1}^{n} (V^E_{k,\text{calc}} - V^E_{k,\text{expt}})^2/(n - n_E)} \tag{10}$$

where n is the number of data points and n_E is the number of coefficients. The correlated results are represented by the dashed curves in Figures 3 and 4.

Table 3. *PVT* Properties of Acetophenone (1) + PEGME-350 (2)

	$T = 298.15$ K		$T = 318.15$ K		$T = 348.15$ K			$T = 298.15$ K		$T = 318.15$ K		$T = 348.15$ K	
P	ρ	$10^4\ \kappa_T$	ρ	$10^4\ \kappa_T$	ρ	$10^4\ \kappa_T$	P	ρ	$10^4\ \kappa_T$	ρ	$10^4\ \kappa_T$	ρ	$10^4\ \kappa_T$
MPa	$g \cdot cm^{-3}$	MPa^{-1}	$g \cdot cm^{-3}$	MPa^{-1}	$g \cdot cm^{-3}$	MPa^{-1}	MPa	$g \cdot cm^{-3}$	MPa^{-1}	$g \cdot cm^{-3}$	MPa^{-1}	$g \cdot cm^{-3}$	MPa^{-1}
w_1[a] = 0.0352 (x_1[b] = 0.1000)													
0.1	1.0817	4.9237	1.0647	5.7498	1.0389	6.5350	30	1.0963	4.3253	1.0805	4.7042	1.0569	5.3867
10	1.0867	4.7069	1.0702	5.3543	1.0453	6.1013	35	1.0986	4.2396	1.0829	4.5668	1.0596	5.2342
15	1.0893	4.6051	1.0729	5.1748	1.0483	5.9045	40	1.1007	4.1576	1.0853	4.4375	1.0623	5.0910
20	1.0916	4.5076	1.0754	5.0072	1.0513	5.7210	45	1.1029	4.0788	1.0876	4.3154	1.0649	4.9558
25	1.0940	4.4143	1.0781	4.8512	1.0541	5.5483	50	1.1051	4.0034	1.0899	4.2004	1.0673	4.8271
w_1 = 0.0765 (x_1 = 0.2000)													
0.1	1.0793	5.2460	1.0620	5.9285	1.0366	6.8160	30	1.0938	4.4436	1.0780	4.8015	1.0545	5.6125
10	1.0843	4.9487	1.0677	5.4990	1.0428	6.3611	35	1.0960	4.3336	1.0804	4.6550	1.0572	5.4528
15	1.0867	4.8115	1.0704	5.3055	1.0459	6.1549	40	1.0982	4.2291	1.0828	4.5177	1.0600	5.3030
20	1.0891	4.6819	1.0729	5.1257	1.0489	5.9623	45	1.1004	4.1299	1.0851	4.3883	1.0625	5.1615
25	1.0915	4.5593	1.0755	4.9584	1.0517	5.7816	50	1.1026	4.0356	1.0874	4.2666	1.0650	5.0274
w_1 = 0.1234 (x_1 = 0.3000)													
0.1	1.0767	5.3490	1.0594	6.1097	1.0337	7.1252	30	1.0912	4.6664	1.0753	4.9437	1.0519	5.7472
10	1.0817	5.1005	1.0650	5.6651	1.0401	6.5970	35	1.0934	4.5697	1.0778	4.7923	1.0546	5.5690
15	1.0842	4.9843	1.0677	5.4648	1.0432	6.3609	40	1.0956	4.4770	1.0802	4.6505	1.0573	5.4025
20	1.0865	4.8733	1.0703	5.2788	1.0462	6.1418	45	1.0978	4.3884	1.0825	4.5167	1.0600	5.2455
25	1.0889	4.7673	1.0729	5.1059	1.0491	5.9376	50	1.1000	4.3033	1.0848	4.3912	1.0624	5.0982
w_1 = 0.1794 (x_1 = 0.4000)													
0.1	1.0732	5.4019	1.0560	6.1638	1.0304	7.1712	30	1.0879	4.6291	1.0721	4.9766	1.0486	5.7969
10	1.0783	5.1170	1.0616	5.7104	1.0367	6.6456	35	1.0902	4.5217	1.0745	4.8229	1.0514	5.6185
15	1.0808	4.9853	1.0644	5.5065	1.0398	6.4098	40	1.0924	4.4194	1.0769	4.6790	1.0540	5.4520
20	1.0832	4.8603	1.0670	5.3173	1.0429	6.1912	45	1.0946	4.3220	1.0793	4.5432	1.0567	5.2950
25	1.0856	4.7414	1.0696	5.1414	1.0457	5.9870	50	1.0967	4.2292	1.0816	4.4161	1.0591	5.1470
w_1 = 0.2472 (x_1 = 0.5000)													
0.1	1.0692	5.5309	1.0520	6.3400	1.0263	7.4198	30	1.0839	4.7392	1.0681	5.1677	1.0445	5.9175
10	1.0742	5.2395	1.0576	5.8945	1.0326	6.8405	35	1.0862	4.6291	1.0706	5.0146	1.0473	5.7255
15	1.0768	5.1046	1.0603	5.6937	1.0357	6.5825	40	1.0884	4.5248	1.0730	4.8707	1.0500	5.5469
20	1.0792	4.9764	1.0630	5.5061	1.0387	6.3442	45	1.0907	4.4254	1.0754	4.7345	1.0526	5.3792
25	1.0816	4.8545	1.0656	5.3317	1.0417	6.1228	50	1.0928	4.3304	1.0777	4.6064	1.0552	5.2216
w_1 = 0.3302 (x_1 = 0.6000)													
0.1	1.0641	5.6685	1.0469	6.5619	1.0210	7.5951	30	1.0790	4.8596	1.0632	5.2896	1.0395	6.0932
10	1.0692	5.3704	1.0526	6.0748	1.0275	7.0180	35	1.0812	4.7477	1.0657	5.1253	1.0423	5.8999
15	1.0718	5.2324	1.0554	5.8568	1.0306	6.7599	40	1.0835	4.6404	1.0681	4.9713	1.0450	5.7201
20	1.0742	5.1020	1.0580	5.6541	1.0337	6.5213	45	1.0857	4.5385	1.0705	4.8259	1.0477	5.5509
25	1.0766	4.9774	1.0607	5.4656	1.0366	6.2993	50	1.0879	4.4410	1.0728	4.6901	1.0503	5.3917
w_1 = 0.4339 (x_1 = 0.7000)													
0.1	1.0578	5.8524	1.0405	6.6829	1.0147	7.7144	30	1.0728	4.9060	1.0570	5.3565	1.0334	6.1432
10	1.0630	5.4988	1.0463	6.1734	1.0213	7.1079	35	1.0751	4.7779	1.0595	5.1862	1.0362	5.9430
15	1.0656	5.3369	1.0491	5.9458	1.0244	6.8380	40	1.0775	4.6565	1.0620	5.0271	1.0390	5.7566
20	1.0680	5.1847	1.0518	5.7346	1.0275	6.5891	45	1.0797	4.5419	1.0644	4.8771	1.0417	5.5818
25	1.0705	5.0411	1.0545	5.5389	1.0305	6.3575	50	1.0819	4.4324	1.0668	4.7369	1.0442	5.4176
w_1 = 0.5676 (x_1 = 0.8000)													
0.1	1.0495	6.0437	1.0322	6.7131	1.0062	7.9190	30	1.0648	4.9808	1.0490	5.4581	1.0253	6.2936
10	1.0548	5.6425	1.0381	6.2352	1.0129	7.2907	35	1.0671	4.8401	1.0515	5.2946	1.0282	6.0869
15	1.0573	5.4605	1.0409	6.0203	1.0161	7.0117	40	1.0694	4.7070	1.0540	5.1412	1.0310	5.8949
20	1.0599	5.2902	1.0437	5.8199	1.0193	6.7539	45	1.0717	4.5818	1.0565	4.9960	1.0337	5.7145
25	1.0623	5.1306	1.0464	5.6330	1.0223	6.5151	50	1.0739	4.4634	1.0588	4.8596	1.0363	5.5453
w_1 = 0.7468 (x_1 = 0.9000)													
0.1	1.0386	6.1923	1.0213	6.9269	0.9950	8.1436	30	1.0542	5.0963	1.0384	5.5851	1.0146	6.3891
10	1.0441	5.7779	1.0272	6.4130	1.0019	7.4600	35	1.0566	4.9515	1.0410	5.4120	1.0176	6.1691
15	1.0467	5.5904	1.0301	6.1833	1.0053	7.1582	40	1.0590	4.8143	1.0435	5.2499	1.0205	5.9657
20	1.0493	5.4149	1.0329	5.9695	1.0085	6.8810	45	1.0613	4.6854	1.0460	5.0967	1.0232	5.7750
25	1.0518	5.2503	1.0357	5.7707	1.0116	6.6251	50	1.0636	4.5635	1.0484	4.9533	1.0259	5.5966

[a] w_1, mass fraction of component 1. [b] x_1, mole fraction of component 1, calculated with the molecular weights of 120.151 and 366.0 for acetophenone and PEGME-350, respectively.

Correlation of Specific Volumes with Equations of State

Both the Flory−Orwoll−Vrij (FOV)[20] and the Schotte[21] EOS were applied to correlate the experimental specific volumes. The definitions of the EOS are as follows.

The FOV EOS:

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{\bar{V}^{1/3}}{\bar{V}^{1/3} - 1} - \frac{1}{\bar{T}\bar{V}} \qquad (11)$$

The Schotte EOS:

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{RT^*}{P^*MV^*}\left(1 - \frac{1}{\bar{V}^{1/3}}\right) + \frac{1}{\bar{V}^{1/3} - 1} - \frac{1}{\bar{T}\bar{V}} \qquad (12)$$

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 obtained by fitting the EOS to the experimental specific volumes of the constituent compounds. Table 6 shows that the

Table 4. Correlated Results of the Tait Equation

		acetophenone (1) + PEG-200 (2)			acetophenone (1) + PEGME-350 (2)		
T/K	x_1	C	D/MPa	$10^4\ \sigma_1{}^a$/(g·cm^{-3})	C	D/MPa	$10^4\ \sigma_1{}^a$/(g·cm^{-3})
298.15	0.0	0.06544	165.09	0.39	0.09009	190.15	0.54
	0.1000	0.08059	197.50	1.06	0.08473	176.48	0.59
	0.2000	0.09215	225.77	0.42	0.08603	179.47	0.38
	0.3000	0.08760	208.34	0.29	0.08906	185.53	0.51
	0.4000	0.08904	205.60	0.44	0.08308	169.67	0.24
	0.5000	0.08404	185.50	0.31	0.08898	181.62	0.45
	0.6000	0.08586	185.34	0.44	0.08888	178.70	0.43
	0.7000	0.08893	183.68	0.45	0.08830	173.40	0.51
	0.8000	0.08566	168.27	0.30	0.08692	166.67	0.37
	0.9000	0.07727	141.62	0.63	0.08516	157.20	0.39
318.15	0.0	0.07459	162.18	0.34	0.07096	128.94	0.57
	0.1000	0.06022	129.24	1.02	0.08253	154.39	0.46
	0.2000	0.08634	190.61	0.31	0.07575	138.12	0.55
	0.3000	0.08373	179.24	0.25	0.08330	153.59	0.42
	0.4000	0.08205	168.86	0.36	0.07885	142.67	0.36
	0.5000	0.07964	158.10	0.54	0.08152	146.60	0.22
	0.6000	0.08455	162.29	0.55	0.07713	135.33	0.36
	0.7000	0.08542	157.40	0.38	0.08011	138.92	0.38
	0.8000	0.08267	144.27	0.36	0.08075	136.53	0.34
	0.9000	0.08674	144.40	0.55	0.08599	141.67	0.40
348.15	0. 0	0.07204	142.29	0.36	0.08873	142.75	0.75
	0.1000	0.08321	160.35	0.43	0.07602	119.00	0.44
	0.2000	0.08544	161.80	0.25	0.08730	139.00	0.60
	0.3000	0.07640	138.18	0.55	0.07850	121.38	0.46
	0.4000	0.08359	148.35	0.48	0.08732	136.54	0.78
	0.5000	0.08591	146.92	0.46	0.08554	132.00	0.38
	0.6000	0.08765	144.79	0.67	0.08366	126.21	0.26
	0.7000	0.08310	128.80	0.34	0.08265	121.69	0.48
	0.8000	0.08465	125.14	0.39	0.08451	121.39	0.40
	0.9000	0.08729	122.14	0.24	0.08408	115.83	0.46

[a] σ_1 defined as in eq 3.

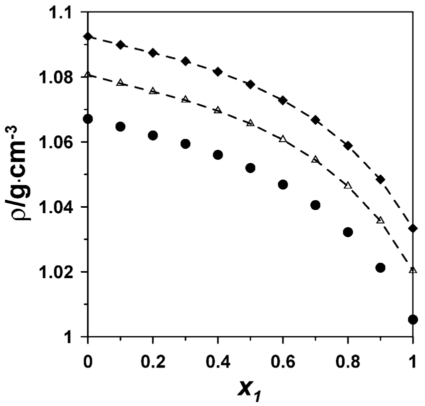

Figure 1. Variation of density with composition for acetophenone (1) + PEGME-350 (2) at 318.15 K under different pressures: ●, 0.1 MPa; △, 25 MPa; ◆, 50 MPa; - - -, calculated values from the Tait equation.

FOV and the Schotte equations correlated the specific volumes to root-mean-square deviations smaller than 0.00032 cm^3·g^{-1} and 0.00025 cm^3·g^{-1}, respectively.

The mixing rules of Schotte[21] were applied to calculate the mixtures' properties which are given by

$$V_{\mathrm{m}}^{*} = \left[M_{\mathrm{m}}\left(\sum_{i=1}^{c}\frac{\Psi_i}{\mathrm{M}_i V_i^{*}}\right)\right]^{-1} \tag{13}$$

$$T_{\mathrm{m}}^{*} = \frac{P_{\mathrm{m}}^{*}}{\sum_{i=1}^{c}\frac{\Psi_i P_i^{*}}{T_i^{*}}} \tag{14}$$

and

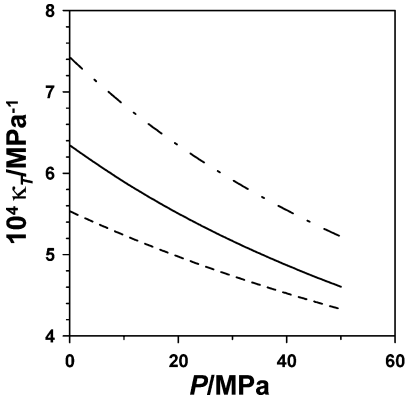

Figure 2. Variation of isothermal compressibility with pressure for equal molar mixture ($x_1 = 0.5$) of acetophenone (1) + PEGME-350 (2) at different temperatures: dashed line, 298.15 K; solid line, 318.15 K; dashed−dot line, 348.15 K.

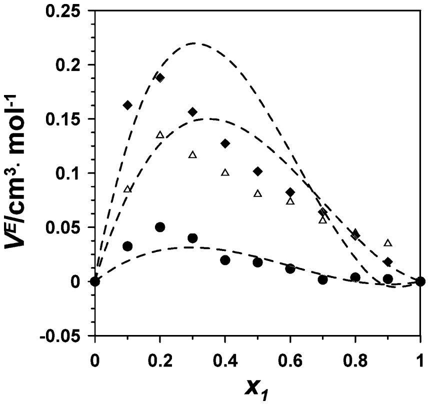

Figure 3. Variations of excess volume with composition for acetophenone (1) + PEG-200 (2) at 318.15 K under different pressures: ●, 0.1 MPa; △, 25 MPa; ◆, 50 MPa; - - -, calculated values from the Redlich−Kister equation.

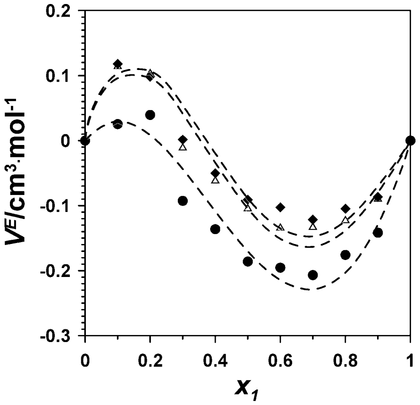

Figure 4. Variations of excess volume with composition for acetophenone (1) + PEGME-350 (2) at 318.15 K under different pressures: ●, 0.1 MPa; △, 25 MPa; ◆, 50 MPa; - - -, calculated values from the Redlich−Kister equation.

$$P_{\mathrm{m}}^{*} = \sum_{i=1}^{c}\sum_{j=1}^{c}\Psi_i\Psi_j P_{ij}^{*} \tag{15}$$

with

$$\Psi_i = \frac{w_i V_i^{*}}{\sum_{i=1}^{c} w_i V_i^{*}} \tag{16}$$

Table 5. Correlated Results of Excess Volumes with the Redlich−Kister Equation

		acetophenone (1) + PEG-200 (2)			acetophenone (1) + PEGME-350 (2)			
T/K	P/MPa	E_0	E_1	$\sigma_2{}^a$/(cm^3·mol^{-1})	E_0	E_1	E_2	$\sigma_2{}^a$/(cm^3·mol^{-1})
298.15	0.1	0.0846	−0.4292	0.018	−0.7645	−1.3499	0.5069	0.047
	10	0.1236	−0.4287	0.019	−0.6927	−1.2052	0.2782	0.045
	15	0.1376	−0.4776	0.024	−0.6009	−1.2378	0.3523	0.041
	20	0.0874	−0.3218	0.019	−0.5856	−1.2261	0.3278	0.038
	25	−0.0166	−0.0604	0.032	−0.5449	−1.1856	0.3588	0.038
	30	0.0269	−0.0608	0.032	−0.5026	−1.1378	0.4348	0.032
	35	0.0125	−0.2832	0.017	−0.4700	−1.0575	0.1881	0.033
	40	0.0215	−0.0907	0.026	−0.4652	−1.1668	0.4447	0.033
	45	−0.0780	0.0420	0.032	−0.4393	−1.1378	0.4844	0.033
	50	−0.1413	0.0885	0.034	−0.3630	−1.1407	0.3495	0.033
318.15	0.1	0.0896	−0.1502	0.018	−0.6812	−1.1010	0.2014	0.032
	10	0.2429	−0.2141	0.030	−0.5658	−1.250	0.6607	0.029
	15	0.2383	−0.2393	0.028	−0.5379	−1.2298	0.7058	0.030
	20	0.4147	−0.3236	0.033	−0.5489	−1.2042	0.8668	0.033
	25	0.5270	−0.4437	0.041	−0.4174	−1.2194	0.7936	0.027
	30	0.5110	−0.4783	0.034	−0.4157	−1.2326	0.7199	0.029
	35	0.5827	−0.5710	0.041	−0.4091	−1.2025	0.7916	0.032
	40	0.6446	−0.7703	0.053	−0.3746	−1.1856	0.8031	0.030
	45	0.6283	−0.6534	0.045	−0.3765	−1.1921	0.8742	0.029
	50	0.6817	−0.9114	0.060	−0.3555	−1.2004	0.8405	0.030
348.15	0.1	0.4546	0.1664	0.026	−0.5276	−1.9322	2.1474	0.068
	10	0.4642	0.2500	0.025	−0.4449	−1.5346	1.5014	0.044
	15	0.4861	0.2222	0.026	−0.3734	−1.6664	1.5786	0.060
	20	0.4861	0.2677	0.032	−0.3309	−1.6162	1.6689	0.059
	25	0.4753	0.2986	0.030	−0.2786	−1.7620	1.9183	0.065
	30	0.3886	0.3377	0.031	−0.2575	−1.7643	1.9389	0.065
	35	0.3954	0.3890	0.034	−0.2254	−1.7678	1.9570	0.066
	40	0.4053	0.3495	0.033	−0.1629	−1.7622	1.7661	0.067
	45	0.3000	0.4840	0.038	−0.1614	−1.7126	1.9831	0.068
	50	0.2561	0.5391	0.041	−0.1597	−1.6889	2.0078	0.063

[a] σ_2 defined as in eq 10.

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})	$10^3\ \sigma_3{}^a$/(cm^3·g^{-1})	P^*/MPa	T^*/K	V^*/(cm^3·g^{-1})	$10^3\sigma_3{}^a$/(cm^3·g^{-1})
acetophenone	633.43	5795.4	0.8060	0.32	646.44	5111.2	0.7944	0.21
PEG-200	735.40	6449.5	0.7542	0.29	761.59	5760.8	0.7455	0.25
PEGME-350	685.51	6102.0	0.7696	0.32	704.49	5411.0	0.7594	0.19

[a] $\sigma_3 = \sqrt{\sum_{k=1}^{n}(V_{k,\mathrm{calc}} - V_{k,\mathrm{expt}})^2/(n-3)}$ where V is the specific volume and n is number of data points.

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

	FOV EOS		Schotte EOS	
mixture (1) + (2)	Δ_{12}	$10^3\ \sigma_4{}^a$/ (cm^3·g^{-1})	Δ_{12}	$10^3\ \sigma_4{}^a$/ (cm^3·g^{-1})
acetophenone + PEG-200	0.0094	0.34	0.0104	0.26
acetophenone + PEGME-350	−0.0048	0.43	−0.0045	0.37

[a] $\sigma_4 = \sqrt{\sum_{k=1}^{n}(V_{k,\mathrm{calc}} - V_{k,\ \mathrm{expt}})^2/(n-1)}$where V is the specific volume and n is number of data points.

and

$$P^*_{ij} = (1 - \Delta_{ij})(P^*_i\, P^*_j)^{0.5} \tag{17}$$

where Ψ_i, M_i, and w_i refer to the segment volume fraction, the number average molecular weight, and the weight fraction of component i, respectively. The parameter Δ_{ij} in eq 17 is a binary interaction constant for i−j pair. Its optimal value was determined from the experimental *PVT* data of each binary system by minimizing the AAD of the calculated specific volumes. Table 7 lists the correlated results, indicating that the Schotte equation, a root-mean-square deviation smaller than 0.00037 cm^3·g^{-1}, is slightly better than the FOV equation, a root-mean-square deviation smaller than 0.00043 cm^3·g^{-1}, for these two oligomeric solution systems. Figure 5 compares the calculated densities with the experimental values for acetophenone + PEG-200. The calculated values, either from the FOV or from the Schotte, agree well with the experimental results of both systems.

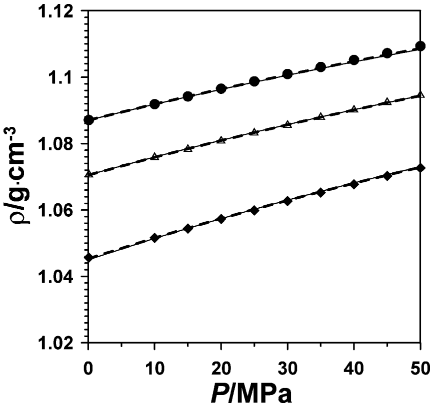

Figure 5. Comparison of calculated results with experimental values for acetophenone (1) + PEG-200 (2) of $x_1 = 0.5$ at different temperatures: ●, 298.15 K; △, 318.15 K; ◆, 348.15 K; —, calculated from the FOV EOS; - - -, calculated from the Schotte EOS.

Conclusions

The *PVT* properties have been measured for two oligomeric solution systems of acetophenone + PEG-200 and acetophenone + PEGME-350 at temperatures from 298.15 K to 348.15 K and pressures up to 50 MPa. The Tait equation presents accurately the pressure effect on the isothermal liquid densities of mixtures at a given composition. The empirical generalized equation, with two characteristic parameters, is capable of satisfactorily correlating the *PVT* data over the whole experimental conditions. The excess volumes were found to be positive in acetophenone + PEG-200 over the entire composition range, whereas those changed from positive to negative as increasing the mole fraction of acetophenone in the mixtures containing PEGME-350. Although slightly better results were obtained from the Schotte EOS, both the FOV and the Schotte EOS correlated the specific volumes of these two oligomeric systems to within the experimental uncertainty.

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