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Volumetric Properties of Binary Tetraethylene Glycol Dimethyl Ether + Heptane Mixtures between (278.15 and 353.15) K and up to 25 MPa

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In this work 885 new experimental densities values are reported for tetraethylene glycol dimethyl ether (TEGDME), heptane, and nine of their mixtures in the compressed liquid phase over the whole composition range, between (278.15 and 353.15) K and for pressures up to 25 MPa or the lowest of either near the appearance of liquid−liquid equilibrium (LLE) of this mixture. The density measurements were performed with an Anton Paar DMA 60/512P vibrating tube densimeter and then correlated by using a Tammann−Tait equation with standard deviations always smaller than or equal to 2×10^{-4} g·cm^{-3}. For the TEGDME + heptane mixtures an increase of pressure at constant temperature favors the appearance of a second liquid phase. The isothermal compressibility, the isobaric thermal expansivity, the internal pressure, and the excess molar volume have been determined from the density data. The isothermal compressibility and the isobaric thermal expansivity decrease when the pressure increases and rise with the temperature increase. The internal pressure increases with the polyether mole fraction. Over the entire temperature and pressure ranges the excess molar volume is positive and asymmetrical toward low TEGDME composition.

Introduction

The temperature dependence of thermophysical properties of systems containing a polar and an apolar component has revealed a surprisingly different and sometimes quite unexpected mixing behavior.[1] Furthermore, the molecular interpretation of these systems has been the subject of controversy.[1,2] First, Grolier et al.[3] and Wilhelm[4] explained the excess properties behavior of this kind of system as due to conformational and molecular orientation changes in the mixture process. Second, Saint-Victor and Patterson[5] proposed a semiquantitative model that involves random and nonrandom contributions. Particularly, for binary liquid mixtures containing a polyether (polar) and an alkane (apolar), different experimental and theoretical studies concerning their thermodynamic properties have been published in recent years.[6−9] The linear polyethers constitute a class of chain molecules similar to the *n*-alkanes but of higher cohesive energy density.[6] Furthermore, molecules containing three or more oxyethylene groups are of particular interest, since they are not completely miscible with long chain *n*-alkanes.[10] The polyether + *n*-alkane systems represent, besides many technically important classes of substance, a particularly interesting family of molecules to check group contribution models[7] and thermodynamic modeling based on equations of state or statistical mechanical models.

To test the prediction and correlation ability of these models, accurate experimental data of thermophysical properties over wide temperature and pressure ranges are necessary. In this sense, the experimental thermodynamic behavior of polyalkylene glycol dimethyl ethers with alkane mixtures has been examined in detail in recent years but only at low pressure. Liquid−liquid coexistence curves for triethylene glycol dimethyl ether (TriEGDME) + alkane and tetraethylene glycol dimethyl ether (TEGDME) + alkane have been analyzed by Treszczanowicz et al.[11] and by Cervantes et al.[12] at normal pressure. The activity coefficients at infinite dilution of TEGDME + alkane have been reported by Arancibia et al.[13] Furthermore, a large experimental database exists[7,9,14−21] of excess molar Gibbs energy, G_m^E, excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, for these mixtures at low pressures. Several authors have found positive and quite large values for the excess molar properties for polyalkylene glycol dimethyl ethers + *n*-alkane mixtures. This fact shows their large deviation from ideality. The excess heat capacity has been reported by Trejo et al.[6] for several polyether + *n*-alkane systems at 298.15 K and by Tovar et al.[8] for TEGDME with heptane for several temperatures. A salient feature of this type of mixtures is their W-shape when the excess heat capacity, C_p^E, is plotted versus the composition. The large H_m^E and G_m^E values that accompany the W-shape of C_p^E indicate that there is a great antipathy between the two components in the mixture, which ultimately, at low temperature, is responsible for the upper critical solution temperature (UCST).[6] Taking into account several experimental data at low pressures, the DISQUAC[7] model and the Prigogine−Flory theory[9,19] have been used in explaining the effect of the molecular structure on the thermodynamic properties of some poly(ethylene glycol) dimethyl ether + *n*-alkane mixtures. It is important to

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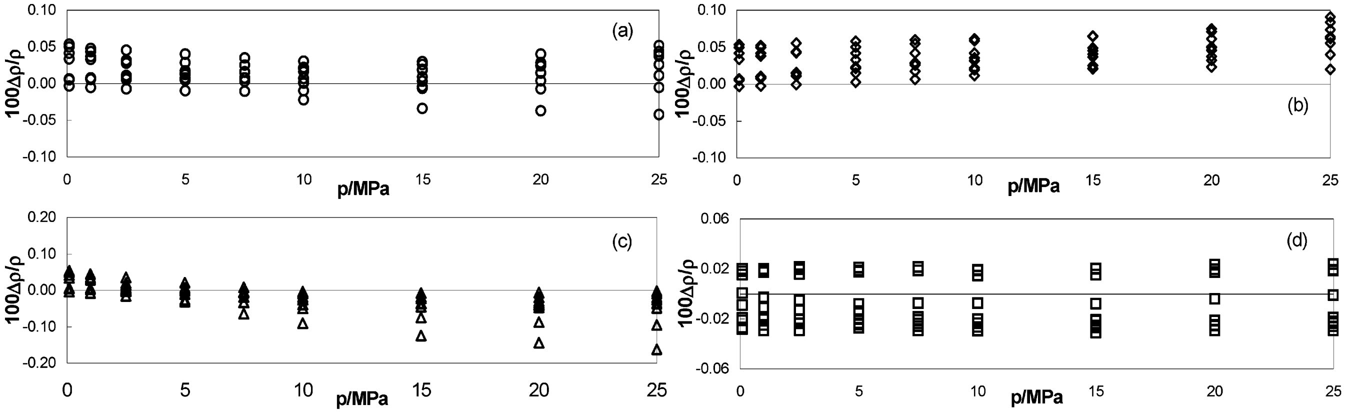

Figure 1. Comparison between the experimental and literature ρpT data at different temperatures between 278.15 and 353.15 K for (a) heptane,[27] (b) heptane,[29] (c) heptane,[30] and (d) TEGDME.[28]

point out that, until now, it appears that there are no articles in the literature dealing with the experimental and theoretical study of these mixtures at high pressure.

Therefore, it is interesting to have supplementary high-pressure measurements for polyether + *n*-alkane mixtures and for polar + apolar systems in general that can be used to complete the interpretation of the thermodynamic properties of these types of mixtures. In the present work extensive density measurements (885 experimental points) were determined for the tetraethylene glycol dimethyl ether (TEGDME) + heptane system over all the composition range, between (278.15 and 353.15) K and for pressures up to 25 MPa. These experimental values were obtained with a vibrating tube densimeter with an experimental uncertainty of $\pm 1 \times 10^{-4}$ g·cm^{-3}. For each mole fraction, the density values have been correlated as temperature and pressure functions by using the Tammann−Tait equation. From the ρpT measurements the isothermal compressibility, the isobaric expansivity, the internal pressure, and the excess molar volumes have been determined. The effect of the systematic variation of the polyether mole fraction on these derived thermodynamic properties has also been analyzed.

Experimental Section

Materials. Heptane (Fluka, puriss ≥99.5%) and TEGDME (Fluka, puriss 99%) were used without purification except drying with Union Carbide 0.4 nm molecular sieves for several days. These chemicals, as well as water (purified using a Milli-Q Plus system, with a resistivity of 18.2 MΩ·cm at 298.15 K), were partially degassed with a Branson 2210 ultrasonic bath before use.

Experimental Method. The Anton Paar DMA 60/512P vibrating tube densimeter was used to determine the density. This type of densimeter can be used to perform measurements in a broad range of temperature from (263.15 to 423.15) K and at pressures from (0 to 70) MPa, but it requires the construction and setup of several pieces of equipment and peripherals. A schematic diagram of the apparatus and the experimental procedure utilized in this work have been described in detail in previous works.[22,23]

We have measured the temperature inside the cell block with an Anton Paar CKT100 platinum resistance thermometer with a resolution of ±0.001 K, which has an accuracy of ±0.01 K. The pressure was measured with a relative manometer HBM-K-PE300, which can measure pressures up to 50 MPa and has an accuracy of ±0.005 MPa. Liquid mixtures were prepared by mass using a precision digital Sartorius 210-P balance with an accuracy of $\pm 5 \times 10^{-5}$ g. The estimated uncertainty in the mole fraction is $\pm 10^{-5}$. In this work we have used the calibration method developed by Lagourette et al.,[24] for which is only necessary to know the density as a temperature and pressure function for a reference fluid (water) and also the temperature dependence of the experimental period for the cell under vacuum. Taking into account the temperature, pressure, mole fraction, period, and the literature water density[25] accuracies, the experimental density uncertainty is $\pm 10^{-4}$ g·cm^{-3}.

Results and Discussion

Densities. Measurements of density were undertaken along nine isotherms between 278.15 K and 353.15 K at 10 K intervals and along nine isobars at pressures up to 25 MPa. A total of 885 experimental points were obtained. The results for nine mixtures of (x)TEGDME + (1 − x)heptane and those of the pure compounds are presented in Table 1.

We have compared our experimental values for the pure compounds with the ρpT literature data reported by several authors.[26−30] Cibulka and Hnědkovský[26,27] in a review paper have analyzed the compatibility between the density measurements carried out by different authors and have reported a set of parameters for the Tammann−Tait equation for each *n*-alkane, which reproduces the density as a temperature and pressure function. In the case of heptane, they have used a database that involves 1576 data points obtained from 21 different primary sources, at temperatures from (188.15 to 523.15) K, and at pressures up to 1078.8 MPa. Cibulka and Hnědkovský have found a root-mean-square deviation of 0.1% for the global correlation over all the database of heptane. Our experimental results present an average absolute deviation of 0.02% with the reference data calculated from their Tammann−Tait correlation. In Figure 1a, we have plotted the deviations between our experimental data and the values calculated from the correlation of Cibulka and Hnědkovský.

Assael et al.[29] have published an overall correlation, which covers densities of *n*-alkanes (from ethane to hexadecane), whose coefficients were determined using 1939 experimental density points. This last correlation reproduces the density values of all the alkanes with an average deviation of 0.1%. In the case of heptane this deviation ranges from 0.05% to 0.10%, depending on the primary sources. The average absolute deviation of our density measurements from those calculated from the correlation proposed by Assael et al. is better than 0.04%, as can be seen in Figure 1b. Finally, our experimental values agree

Table 1. Experimental Values of Densities, ρ (g·cm^{-3}), for (x)TEGDME + (1 − x)Heptane at Different Temperatures, T, and Pressures, p

		ρ/g·cm^{-3} at the following values of T/K								
x	p/MPa	278.15	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15
0.000 00	0.100	0.6963	0.6921	0.6837	0.6753	0.6666	0.6576	0.6489	0.6398	0.6306
	1.000	0.6970	0.6929	0.6846	0.6762	0.6676	0.6587	0.6500	0.6411	0.6320
	2.500	0.6983	0.6942	0.6859	0.6777	0.6691	0.6604	0.6518	0.6431	0.6342
	5.000	0.7003	0.6963	0.6882	0.6801	0.6717	0.6631	0.6548	0.6463	0.6378
	7.500	0.7023	0.6983	0.6904	0.6824	0.6742	0.6658	0.6576	0.6494	0.6411
	10.000	0.7042	0.7002	0.6925	0.6847	0.6766	0.6684	0.6604	0.6524	0.6443
	15.000	0.7079	0.7040	0.6966	0.6890	0.6812	0.6733	0.6656	0.6580	0.6503
	20.000	0.7114	0.7076	0.7004	0.6930	0.6855	0.6779	0.6704	0.6631	0.6557
	25.000	0.7147	0.7111	0.7039	0.6969	0.6895	0.6821	0.6749	0.6679	0.6608
0.105 04	0.100	0.7439	0.7396	0.7313	0.7226	0.7137	0.7049	0.6954	0.6867	0.6775
	1.000	0.7446	0.7403	0.7321	0.7235	0.7146	0.7060	0.6965	0.6879	0.6788
	2.500	0.7458	0.7416	0.7335	0.7249	0.7162	0.7077	0.6983	0.6898	0.6809
	5.000	0.7478	0.7437	0.7357	0.7273	0.7187	0.7103	0.7011	0.6929	0.6842
	7.500	0.7497	0.7456	0.7378	0.7295	0.7211	0.7129	0.7039	0.6958	0.6874
	10.000	0.7516	0.7476	0.7399	0.7317	0.7235	0.7153	0.7065	0.6987	0.6904
	15.000	0.7552	0.7513	0.7439	0.7359	0.7280	0.7201	0.7115	0.7040	0.6961
	20.000	0.7586	0.7548	0.7476	0.7398	0.7322	0.7246	0.7162	0.7090	0.7013
	25.000	0.7619	0.7582	0.7512	0.7436	0.7361	0.7287	0.7206	0.7136	0.7062
0.198 47	0.100	0.7834	0.7790	0.7702	0.7614	0.7525	0.7432	0.7343	0.7251	0.7156
	1.000	0.7841	0.7798	0.7710	0.7623	0.7533	0.7442	0.7353	0.7262	0.7168
	2.500	0.7853	0.7810	0.7723	0.7637	0.7548	0.7458	0.7370	0.7280	0.7188
	5.000	0.7872	0.7830	0.7745	0.7659	0.7572	0.7483	0.7397	0.7309	0.7220
	7.500	0.7891	0.7849	0.7766	0.7681	0.7595	0.7508	0.7423	0.7338	0.7250
	10.000	0.7910	0.7868	0.7786	0.7702	0.7617	0.7532	0.7449	0.7365	0.7280
	15.000		0.7904	0.7825	0.7743	0.7661	0.7578	0.7498	0.7416	0.7335
	20.000			0.7861	0.7782	0.7702	0.7622	0.7543	0.7464	0.7386
	25.000			0.7896	0.7819	0.7741	0.7663	0.7586	0.7510	0.7434
0.299 50	0.100	0.8225	0.8180	0.8090	0.8001	0.7911	0.7820	0.7725	0.7638	0.7545
	1.000	0.8231	0.8187	0.8097	0.8009	0.7920	0.7830	0.7735	0.7648	0.7556
	2.500	0.8243	0.8199	0.8109	0.8023	0.7934	0.7845	0.7751	0.7666	0.7575
	5.000	0.8261	0.8218	0.8129	0.8044	0.7957	0.7869	0.7777	0.7694	0.7605
	7.500	0.8279	0.8237	0.8149	0.8065	0.7980	0.7893	0.7802	0.7721	0.7634
	10.000	0.8297	0.8255	0.8169	0.8085	0.8001	0.7916	0.7827	0.7747	0.7661
	15.000	0.8332	0.8290	0.8206	0.8125	0.8043	0.7960	0.7873	0.7796	0.7713
	20.000	0.8365	0.8324	0.8242	0.8162	0.8083	0.8002	0.7917	0.7842	0.7762
	25.000		0.8357	0.8276	0.8198	0.8121	0.8042	0.7958	0.7886	0.7809
0.402 13	0.100	0.8588	0.8544	0.8453	0.8366	0.8275	0.8182	0.8092	0.8000	0.7904
	1.000	0.8594	0.8551	0.8461	0.8374	0.8283	0.8191	0.8101	0.8010	0.7915
	2.500	0.8605	0.8562	0.8473	0.8386	0.8297	0.8205	0.8117	0.8026	0.7933
	5.000	0.8623	0.8581	0.8492	0.8407	0.8318	0.8228	0.8141	0.8052	0.7961
	7.500	0.8641	0.8599	0.8511	0.8427	0.8339	0.8251	0.8166	0.8078	0.7989
	10.000	0.8658	0.8617	0.8530	0.8447	0.8360	0.8273	0.8189	0.8102	0.8015
	15.000	0.8692	0.8651	0.8566	0.8485	0.8401	0.8316	0.8234	0.8150	0.8065
	20.000	0.8724	0.8684	0.8601	0.8521	0.8439	0.8357	0.8277	0.8194	0.8112
	25.000	0.8755	0.8716	0.8634	0.8556	0.8476	0.8395	0.8317	0.8237	0.8157
0.509 97	0.100	0.8941	0.8896	0.8805	0.8715	0.8624	0.8533	0.8439	0.8351	0.8257
	1.000	0.8948	0.8902	0.8811	0.8722	0.8632	0.8541	0.8448	0.8360	0.8267
	2.500	0.8958	0.8913	0.8823	0.8735	0.8645	0.8554	0.8462	0.8375	0.8284
	5.000	0.8976	0.8931	0.8841	0.8755	0.8666	0.8577	0.8485	0.8401	0.8310
	7.500	0.8993	0.8948	0.8859	0.8774	0.8687	0.8598	0.8508	0.8425	0.8336
	10.000	0.9009	0.8965	0.8877	0.8793	0.8707	0.8619	0.8530	0.8448	0.8361
	15.000	0.9041	0.8998	0.8912	0.8829	0.8746	0.8660	0.8573	0.8494	0.8409
	20.000	0.9072	0.9029	0.8945	0.8865	0.8783	0.8699	0.8613	0.8537	0.8454
	25.000	0.9102	0.9060	0.8977	0.8899	0.8818	0.8736	0.8652	0.8578	0.8497
0.590 95	0.100	0.9190	0.9144	0.9053	0.8962	0.8869	0.8784	0.8683	0.8593	0.8501
	1.000	0.9196	0.9151	0.9059	0.8969	0.8877	0.8792	0.8691	0.8602	0.8511
	2.500	0.9206	0.9161	0.9070	0.8980	0.8889	0.8805	0.8703	0.8617	0.8526
	5.000	0.9223	0.9178	0.9088	0.9000	0.8908	0.8826	0.8725	0.8641	0.8552
	7.500	0.9239	0.9195	0.9106	0.9018	0.8928	0.8847	0.8747	0.8664	0.8576
	10.000	0.9255	0.9211	0.9124	0.9036	0.8947	0.8867	0.8768	0.8687	0.8600
	15.000	0.9287	0.9243	0.9158	0.9072	0.8985	0.8907	0.8809	0.8730	0.8646
	20.000	0.9317	0.9274	0.9190	0.9106	0.9021	0.8944	0.8849	0.8772	0.8689
	25.000	0.9346	0.9304	0.9221	0.9139	0.9055	0.8980	0.8886	0.8812	0.8730
0.698 27	0.100	0.9499	0.9454	0.9360	0.9269	0.9180	0.9089	0.8990	0.8904	0.8811
	1.000	0.9505	0.9460	0.9366	0.9276	0.9187	0.9097	0.8998	0.8912	0.8820
	2.500	0.9515	0.9470	0.9377	0.9287	0.9199	0.9109	0.9011	0.8926	0.8835
	5.000	0.9531	0.9486	0.9394	0.9305	0.9218	0.9129	0.9033	0.8949	0.8859
	7.500	0.9546	0.9502	0.9411	0.9323	0.9237	0.9149	0.9053	0.8971	0.8883
	10.000	0.9561	0.9518	0.9428	0.9341	0.9256	0.9168	0.9074	0.8993	0.8905
	15.000	0.9592	0.9549	0.9460	0.9375	0.9292	0.9206	0.9114	0.9034	0.8949
	20.000	0.9621	0.9579	0.9491	0.9408	0.9326	0.9242	0.9151	0.9074	0.8991
	25.000	0.9649	0.9607	0.9522	0.9439	0.9360	0.9277	0.9187	0.9112	0.9031

Table 1. (Continued)

		ρ/g·cm^{-3} at the following values of T/K								
x	p/MPa	278.15	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15
0.801 14	0.100	0.9776	0.9728	0.9634	0.9543	0.9453	0.9361	0.9264	0.9176	0.9083
	1.000	0.9782	0.9734	0.9639	0.9550	0.9460	0.9367	0.9272	0.9184	0.9091
	2.500	0.9790	0.9744	0.9649	0.9561	0.9471	0.9379	0.9284	0.9198	0.9106
	5.000	0.9806	0.9759	0.9666	0.9578	0.9490	0.9398	0.9305	0.9220	0.9128
	7.500	0.9821	0.9775	0.9682	0.9595	0.9508	0.9416	0.9325	0.9241	0.9151
	10.000	0.9836	0.9790	0.9698	0.9613	0.9525	0.9434	0.9344	0.9262	0.9172
	15.000	0.9865	0.9820	0.9729	0.9645	0.9560	0.9471	0.9382	0.9302	0.9214
	20.000	0.9893	0.9849	0.9759	0.9677	0.9593	0.9506	0.9418	0.9340	0.9254
	25.000	0.9921	0.9877	0.9789	0.9708	0.9625	0.9539	0.9453	0.9376	0.9293
0.901 99	0.100	1.0024	0.9977	0.9884	0.9794	0.9703	0.9609	0.9512	0.9426	0.9332
	1.000	1.0029	0.9983	0.9890	0.9800	0.9710	0.9616	0.9519	0.9433	0.9340
	2.500	1.0038	0.9992	0.9899	0.9810	0.9720	0.9627	0.9531	0.9446	0.9353
	5.000	1.0053	1.0007	0.9915	0.9827	0.9738	0.9646	0.9550	0.9467	0.9375
	7.500	1.0067	1.0022	0.9931	0.9843	0.9756	0.9664	0.9570	0.9487	0.9396
	10.000	1.0082	1.0037	0.9946	0.9859	0.9773	0.9682	0.9589	0.9507	0.9417
	15.000	1.0110	1.0066	0.9977	0.9891	0.9806	0.9717	0.9625	0.9546	0.9458
	20.000	1.0137	1.0094	1.0006	0.9922	0.9839	0.9751	0.9660	0.9583	0.9497
	25.000	1.0164	1.0121	1.0034	0.9951	0.9870	0.9784	0.9694	0.9618	0.9534
1.000 00	0.100	1.0251	1.0204	1.0111	1.0021	0.9929	0.9836	0.9741	0.9650	0.9557
	1.000	1.0256	1.0209	1.0116	1.0027	0.9935	0.9843	0.9748	0.9658	0.9565
	2.500	1.0265	1.0218	1.0126	1.0037	0.9946	0.9853	0.9760	0.9670	0.9578
	5.000	1.0279	1.0233	1.0141	1.0053	0.9963	0.9871	0.9779	0.9690	0.9599
	7.500	1.0293	1.0247	1.0156	1.0069	0.9979	0.9889	0.9798	0.9710	0.9620
	10.000	1.0307	1.0261	1.0171	1.0085	0.9996	0.9906	0.9816	0.9729	0.9640
	15.000	1.0334	1.0289	1.0200	1.0115	1.0028	0.9940	0.9851	0.9766	0.9679
	20.000	1.0361	1.0316	1.0229	1.0145	1.0060	0.9973	0.9885	0.9802	0.9717
	25.000	1.0387	1.0343	1.0256	1.0174	1.0090	1.0005	0.9918	0.9837	0.9753

with the data reported by Malhotra et al.[30] within an average deviation better than 0.02%, as show Figure 1c. For pure TEGDME, Comuñas et al.[28] have recently reported density values for temperatures ranging from 283.15 to 353.15 K and at pressures up to 60 MPa. We have compared our values with those reported by these authors, finding an average absolute deviation of 0.02%, as is shown in Figure 1d.

As it can be observed in Table 1, we report any experimental data for $x = 0.198\ 47$ over the 278.15 K isotherm and at (15, 20, and 25) MPa, and for 283.15 K at (20 and 25) MPa. The same fact occurs for $x = 0.299\ 50$ at 278.15 K and for 25 MPa. At these pTx conditions, we observed large fluctuations in the vibration period. This fact is due to the appearance of liquid−liquid equilibria (LLE). Unfortunately, with the experimental equipment utilized in this work we cannot determine reliable values for density under these conditions; nevertheless, we can detect the existence of two phases from the period fluctuations. The experimental liquid−liquid coexistence curves at atmospheric pressure of binary polyether + n-alkane (decane, dodecane, and hexadecane) mixtures have been published by Treszczanowicz et al.[11] From the experimental values reported by these authors it can be concluded that the upper critical solubility temperature (UCST), T_c, increases when the molecular size of each component is raised, as occurs for components of low affinity. The asymmetry of the coexistence curves increases almost linearly when the number of carbon atoms of the n-alkane increases. Taking into account this alkane chain length dependence, the critical composition and temperature of the mixture (x)TEGDME + (1 − x)heptane can be estimated from the liquid−liquid coexistence curves reported by Treszczanowicz et al.[11] The rough values one gets are $x_c = 0.25$ and $T_c = 276$ K, at atmospheric pressure. From our experimental results up to 25 MPa, we have found that an increase of pressure favors the appearance of a second liquid phase for the studied system. This is in agreement with the fact that for mixtures with positive excess molar volumes, as in the present case,[16,19] the UCST increases when the pressure increases, as can be concluded from thermodynamic relations.[31] Over all the pTx range, except in the liquid−liquid coexistence region, the density behavior of the mixtures is standard, ρ is observed to decrease with the increase of T, and ρ increases when the pressure rises, as it is shown in Figure 2 for $p = 20$ MPa and $T = 333.15$ K. Furthermore, the results for a given composition show a pressure and temperature dependence similar to that of the pure components, varying monotonically with the composition x, from pure heptane up to TEGDME.

The ρpT measurement values in the compressed liquid phase were represented for each mole fraction with the following modified Tammann−Tait equation:[27]

$$\rho(T,p,C,B) = \frac{\rho(T,p_{\mathrm{ref}}(T))}{1 - C\ln\left(\dfrac{(B(T)+p)}{B(T)+p_{\mathrm{ref}}(T)}\right)} \tag{1}$$

where $\rho(T,p_{\mathrm{ref}}(T))$ is the temperature dependence of the density at the reference pressure (in this case atmospheric pressure) and is given by

$$\rho(T,\ 0.1\ \mathrm{MPa}) = A_0 + A_1T + A_2T^2 \tag{2}$$

The denominator of eq 1 changes with both temperature and pressure. The parameter C was assumed to be temperature independent, and for $B(T)$, we have used the following polynomial function:

$$B(T) = B_0 + B_1T + B_2T^2 \tag{3}$$

The values of A_i, B_i, and C were determined by fitting our experimental data in the whole pT range to eq 1 using a Marquardt−Levenberg type algorithm.[32] For all the mixtures, the standard deviation from the Tammann−Tait correlation is less than or equal to 2×10^{-4} g·cm^{-3}. The obtained A_i, B_i, and C values and the standard deviations

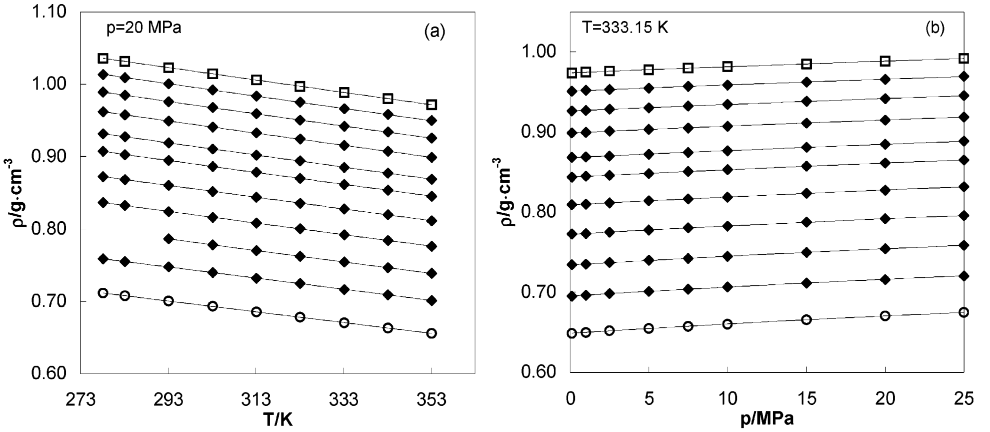

Figure 2. Experimental values of the densities for (x)TEGDME + (1 − x)heptane versus (a) the temperature, T, at 20 MPa and (b) the pressure, p, at 333.15 K: ○, heptane; ◆, the following mole fractions of TEGDME (0.10504, 0.19847, 0.29950, 0.40213, 0.50997, 0.59095, 0.69827, 0.80114, and 0.90199); □, TEGDME.

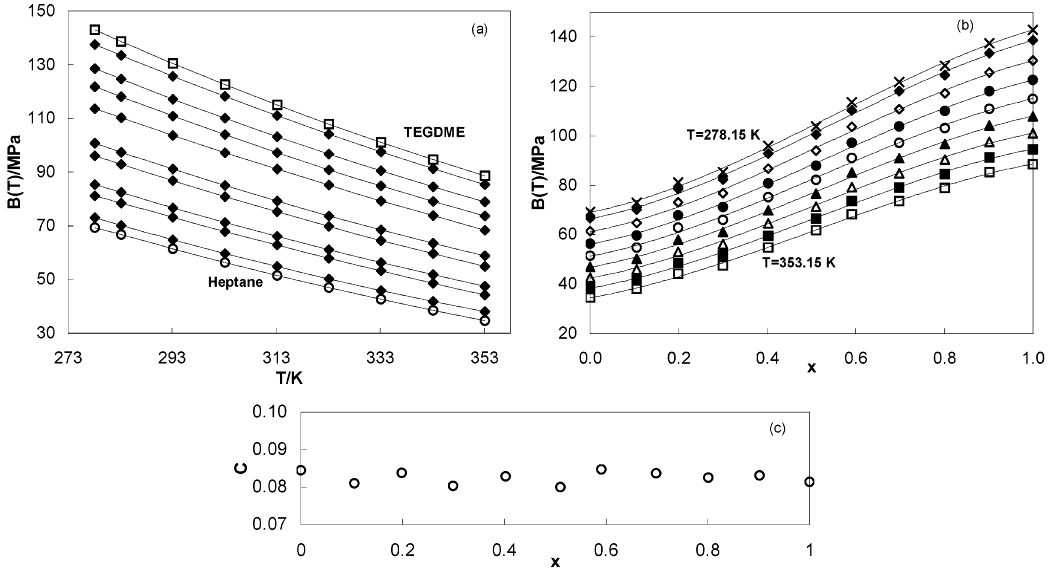

Figure 3. Dependence of the parameters $B(T)$ and C of the Tammann−Tait equation: (a) $B(T)$ versus the temperature, T, for the pure components and for nine mole fractions; (b) $B(T)$ versus mole fraction of TEGDME for nine temperatures, T; (c) C versus mole fraction of TEGDME.

Table 2. Coefficients, A_i, B_i, and C, and Standard Deviation, σ, of the Fit of Eq 1 for (x)TEGDME + (1 − x)Heptane

	heptane	$x = 0.105\,04$	$x = 0.198\,47$	$x = 0.299\,5$	$x = 0.402\,13$	$x = 0.509\,97$
A_0/g·cm^{-3}	0.877 36	0.933 93	0.987 26	1.053 67	1.072 46	1.137 72
$-A_1$/(×10^3 g·cm^{-3}·K^{-1})	0.4739	0.5223	0.5992	0.7719	0.6565	0.8477
$-A_2$/(×10^6 g·cm^{-3}·K^{-2})	0.64	0.58	0.48	0.21	0.40	0.10
B_0/MPa	309.9627	332.7894	298.7072	344.0423	366.7015	395.7181
$-B_1$/MPa·K^{-1}	1.1808	1.3038	1.0090	1.2648	1.3073	1.4557
B_2/(×10^3 MPa·K^{-2})	1.136	1.329	0.816	1.204	1.202	1.421
C	0.084 442	0.081 045	0.083 803	0.080 298	0.082 924	0.079 970
σ/(×10^4 g·cm^{-3})	1	2	1	1	1	1

	$x = 0.590\,95$	$x = 0.698\,27$	$x = 0.801\,14$	$x = 0.901\,99$	TEGDME
A_0/g·cm^{-3}	1.154 24	1.202 55	1.239 34	1.257 43	1.271 81
$-A_1$/(×10^3 g·cm^{-3}·K^{-1})	0.7888	0.9006	0.9569	0.9124	0.8580
$-A_2$/(×10^6 g·cm^{-3}·K^{-2})	0.21	0.03	−0.06	0.02	0.11
B_0/MPa	377.8850	448.5700	458.5824	481.2902	521.7463
$-B_1$/MPa·K^{-1}	1.2232	1.5939	1.6014	1.6633	1.8635
B_2/(×10^3 MPa·K^{-2})	0.982	1.507	1.490	1.535	1.803
C	0.0847 63	0.083 673	0.082 502	0.083 070	0.081 375
σ/(×10^4 g·cm^{-3})	2	2	2	2	1

are listed in Table 2. The function $B(T)$ is plotted in Figure 3, where it is shown that B decreases with the temperature increase and rises with the TEGDME mole fraction. Figure 3 shows also that the C parameter is almost constant over all the mole fraction range.

Derived Properties. Using the Tammann−Tait equation with the parameters presented in Table 2, the isothermal compressibility, $\kappa_T = (1/\rho)(\partial\rho/\partial p)_T$, the isobaric thermal expansivity, $\alpha_p = -(1/\rho)(\partial\rho/\partial T)_p$, and the internal pressure, $\pi = T(\partial p/\partial T)_v - p$, have been determined over

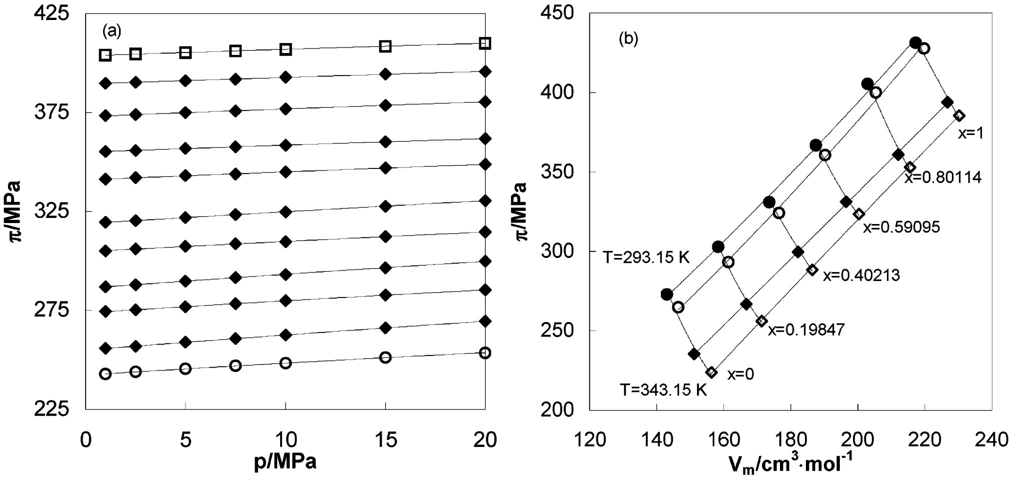

Figure 4. Internal pressure, π, for (x)TEGDME + $(1 - x)$heptane: (a) against pressure at $T = 323.15$ K and for different mole fractions (○, heptane; □, TEGDME); (b) against volume for several mixtures, at two isotherms (circles, 293.15 K; diamonds, 343.15 K) and for two pressures (◇ and ○, 1 MPa; ◆ and ●, 20 MPa).

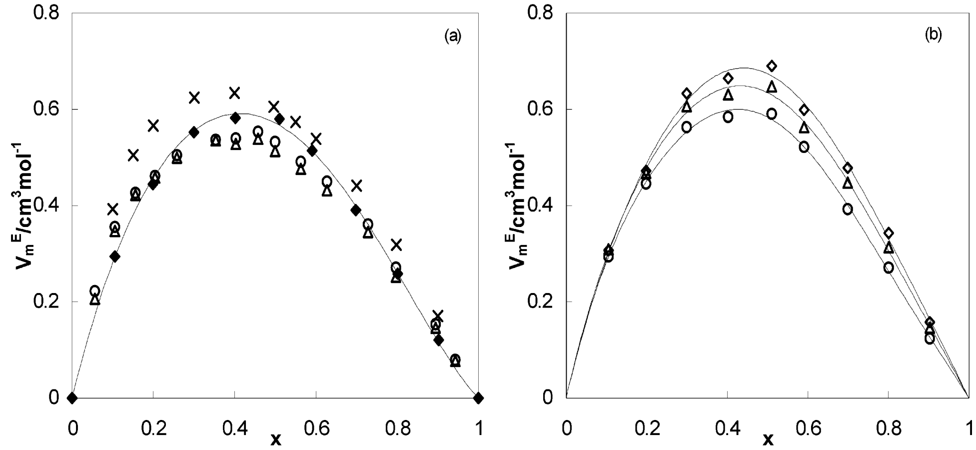

Figure 5. Experimental values of excess molar volumes for (x)TEGDME + $(1 - x)$heptane versus the mole fraction: (a) at atmospheric pressure for 298.15 K (×[19] and △[17]), 293.15 K (◆, this work), and 288.15 K (○[17]); (b) at 293.15 K for different pressures (○, 1 MPa; △, 10 MPa; ◇, 25 MPa).

the whole temperature and pressure ranges. The estimated uncertainties of these properties are $\pm 0.03 \times 10^{-4}$ MPa^{-1}, $\pm 0.2 \times 10^{-4}$ K^{-1}, and ±1 MPa, respectively.

Isothermal compressibility and isobaric thermal expansivity decrease when the pressure increases (17% for κ_T and 12% for α_p at 303.15 K) and rise with the temperature increase. The temperature dependence of the isothermal compressibilities, calculated from the Tammann−Tait equation, is determined mainly by the temperature dependence of the parameter $B(T)$ and is certainly the most direct way to obtain reliable isothermal compressibility values.[33]

The internal pressure is positive for the mixtures and pure compounds, increasing along an isotherm when the pressure rises (about 2% for TEGDME and 4% for heptane). This fact is shown in Figure 4a, where the internal pressure values are plotted at 323.15 K versus the pressure over the entire mole fraction interval. Plots of the internal pressure for pure liquids and for four of their mixtures as functions of molar volume over two isotherms and two isobars are shown in Figure 4b. An inspection of this figure shows that the values of the internal pressure for the pure compounds and their mixtures decrease when the temperature increases or, in other words, cohesive forces[34] decrease when the temperature increases. The randomness of the distribution of the molecules in the mixture increases when the temperature rises, and this increment decreases the attractive contribution to the internal pressure.[23] We can also see that, when the volume is increased along an isobar, the internal pressure increases more rapidly than when the volume rises along an isotherm. It is also observed that the internal pressure values of TEGDME are greater than those of heptane and, as expected, they increase with the mole fraction of TEGDME, ranging from 224 MPa for pure heptane at 343.15 K and 1 MPa to 337 MPa for pure TEGDME at 283.15 K and 20 MPa. This is due to the presence of the polar group ($\mu = 2.4$ D for TEGDME,[35] while μ is close to 0 for heptane[36]). This behavior has also been found in a previous work for other mixtures.[23]

Excess Molar Volumes. From experimental density data, the excess molar volume, V_m^E, at each pressure, p, and temperature, T, has been calculated using the following relation:

$$V_m^E(T,p,x) = xM_1\left(\frac{1}{\rho_x(T,p)} - \frac{1}{\rho_1(T,p)}\right) + (1 - x)M_2\left(\frac{1}{\rho_x(T,p)} - \frac{1}{\rho_2(T,p)}\right) \quad (4)$$

where M_i and ρ_i denote, respectively, the pure liquid's molecular mass and density and x and ρ are respectively the mixture's mole fraction and the density.

Treszanowicz et al.[19] and Romaní et al.[17] have measured the excess molar volumes at atmospheric pressure for TEGDME + heptane mixtures at 298.15 K and at (278.15, 288.15, 298.15, and 308.15) K, respectively. Their values at 298.15 K present percentual deviations ranging from 8% to 15%. Figure 5a shows our experimental V_m^E values at 0.1 MPa and at 293.15 K together with the values reported by Treszczanowicz et al.[19] at 298.15 K and by Romaní et al.[17] at (298.15 and 288.15) K at the same pressure. As can be seen in this figure, our excess molar volume values are between the data set reported by these authors.

In Figure 5b, our experimental excess molar volumes have been plotted against the TEGDME mole fraction at 293.15 K and for several pressures. At all the temperatures and pressures this excess property is positive and asymmetrical toward low polyether composition. It is observed that the excess molar volumes rise when the temperature decreases, as Romaní et al.[17] have found at atmospheric pressure. On the other hand, it can be concluded that the excess molar volumes rise when the pressure increases at a given temperature. This behavior can be due to a great antipathy between the two components in the mixture.[6] The V_m^E dependence on pressure is about 3% per megapascal, and that on temperature is close to 0.3% per degree kelvin.

Conclusions

The volumetric behavior of tetraethylene glycol dimethyl ether + heptane mixtures has been analyzed in wide temperature and pressure ranges. In the literature, there are not experimental data at high pressure concerning polyalkylene glycol dimethyl ethers + *n*-alkane mixtures. The Tammann−Tait equation correlated the experimental $p\rho T$ data with standard deviations lower than or equal to 2×10^{-4} g·cm^{-3}. From our experimental results up to 25 MPa, we have found that an increase of pressure at constant temperature favors the appearance of a second liquid phase for the studied system. The internal pressure values of TEGDME are greater than those of heptane and, as expected, increase with the mole fraction of TEGDME; this is due to the presence of the polar group. It is also observed that the excess molar volumes rise when the temperature decreases, as other authors have found at atmospheric pressure. On the other hand, it can be concluded that the excess molar volumes rise when the pressure increases at a given temperature, with this variation being more noticeable than those found with the temperature. It is hoped that the data will aid the test of group contribution models and equations of state of polyalkylglycol + alkane mixtures.

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