

Experimental (P , V , T , x) Data for the Mixture Ethyl Nonafluorobutyl Ether + n -Hexane

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Experimental high-pressure density data for the binary mixture of methyl nonafluorobutyl ether + hexane were determined. The pressure range considered was 0.1 to 25 MPa, and densities were measured along three isotherms, at temperatures of (283.15, 298.15, and 313.15) K. An Anton Paar DMA 4500 vibrating-tube densimeter, connected to a high-pressure measuring cell, was used for density measurement. Experimental data for the mixture were fitted using a modified Tait equation. Excess molar volumes were as well calculated and correlated, using a modified Redlich–Kister equation, which includes a temperature- and pressure-dependent factor.

Introduction

Hydrofluoroethers (HFEs) have been identified as environmentally friendly substitutes to other halogenated substances, as for instance chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), or perfluorocarbons (PFCs). Over the past few years, many research papers addressing the HFEs suitability for practical purposes have been published.^{1–3} Among the applications where this type of products are already being used, electronic and magnetic devices cleaning, foaming or low temperature heat exchange refrigerating can be outlined. The main reasons supporting the spreading of their use are their zero ozone-depleting potential (ODP), low global warming potential (GWP), short atmospheric lifetimes, and very low toxicity, as reported recently by Tsai.⁴ Among these compounds, the so-called segregated HFEs (those molecules where an ether functional group links an aliphatic and a perfluorinated chain) have been pointed out for their useful profile, but experimental thermophysical data are very scarce in the literature, so an adequate description of their complete thermodynamic behavior is not possible so far. In previous works, our research group has presented experimental high-pressure densities⁵ and speeds of sound⁶ for methyl and ethyl nonafluorobutyl ether. The mixing volumetric behavior of these compounds has been studied as well previously for the methyl nonafluorobutyl ether + n -hexane binary.⁷ A paper describing the volumetric behavior of pure segregated HFEs using PC–SAFT EOS has also been published.⁸ As a continuation, in this paper the mixing behavior of ethyl nonafluorobutyl + n -hexane is studied. With this aim, experimental ρPT values have been measured and correlated using a modified Tait equation, keeping a glance as well on the highly non-ideal volumetric behavior of this asymmetric mixture through calculation of excess molar volumes. These measured mixture compressed liquid densities are a useful test to study the performance of any theoretical method (equations of state or group-contribution models), when applied to thermodynamic characterization of this kind of molecules. Many of these theoretical methods yield fairly good estimations on saturation conditions even for these halogenated compounds, despite the big size of the molecules and their marked non-

ideal behavior, but fail to describe the compressed liquid properties. This fact makes these theoretical methods useless to estimate temperature or pressure derivative properties (speed of sound or heat capacity, for instance), and so compressed liquid thermophysical properties data turn out to be very useful to test and tune such kind of models.

Experimental Section

n -Hexane was supplied by Fluka (mass purity >99.5 %). Ethyl nonafluorobutyl ether was supplied by TCI (Tokyo Chemicals Industries, Japan), with a purity of 99.8 %. This last product is actually a mixture of two inseparable structural isomers, with the same physical properties, containing ethyl nonafluorobutyl ether ($\text{CF}_3(\text{CF}_2)_3\text{OCH}_2\text{CH}_3$, CAS Registry No. 163702-05-4) and ethyl nonafluoroisobutyl ether ($(\text{CF}_3)_2\text{CFCH}_2\text{OCH}_2\text{CH}_3$, CAS Registry No. 163702-06-5). Both products were degassed in an ultrasound bath, stored over molecular sieves to remove moisture traces, and kept in inert argon atmosphere. No further purification methods were applied.

Both pure liquid and mixture densities were measured using a vibrating-tube Anton Paar DMA 4500 densimeter, which provides a density repeatability of $10^{-5} \text{ g}\cdot\text{cm}^{-3}$, connected to an external Anton Paar 512 P high-pressure measuring cell, which enables density measurements up to 70 MPa. Temperature stability is kept through a PolyScience 9510 circulating fluid thermostatic bath, and temperature is measured using a CKT-100 platinum probe placed by the measuring cell, which ensures an uncertainty lower than $5\cdot 10^{-2} \text{ K}$. Pressure is generated and controlled using a Ruska 7610 pressure controller, which ensures a pressure stability of $2\cdot 10^{-3} \text{ MPa}$. The hydraulic fluid (oil) is separated from the sample using a Teflon membrane separator provided by Pressurements. A right pressure transmission through the separator membrane is ensured by measuring the sample pressure with a SI digital manometer, with an uncertainty of 10^{-2} MPa . Mixture samples were prepared by weight using an AND HM 202 balance, with an accuracy of 10^{-4} g , which gives through propagation calculation an estimated uncertainty of 10^{-4} in mole fraction determination.

The experimental technique has been previously described in detail.⁹ The densimeter calibration was performed applying the method proposed by Lagourette et al.¹⁰ using water and vacuum as calibrating fluids. This method enables obtaining a

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Table 1. Experimental Densities, $\rho/\text{g}\cdot\text{cm}^{-3}$, for the Mixture Ethyl Nonfluorobutyl Ether (1) + Hexane (2)

<i>P</i> /MPa	$\rho/\text{g}\cdot\text{cm}^{-3}$								
	<i>T</i> = 283.15 K	<i>T</i> = 298.15 K	<i>T</i> = 313.15 K	<i>T</i> = 283.15 K	<i>T</i> = 298.15 K	<i>T</i> = 313.15 K	<i>T</i> = 283.15 K	<i>T</i> = 298.15 K	<i>T</i> = 313.15 K
		$x_1 = 0.0532$			$x_1 = 0.0989$			$x_1 = 0.1885$	
0.1	0.7224	0.7074	0.6917	0.7668	0.7506	0.7336	0.8513	0.8328	0.8131
1	0.7234	0.7084	0.6938	0.7680	0.7517	0.7359	0.8525	0.8341	0.8156
2	0.7245	0.7097	0.6951	0.7693	0.7532	0.7374	0.8539	0.8358	0.8174
3	0.7256	0.7109	0.6965	0.7705	0.7544	0.7389	0.8553	0.8373	0.8192
4	0.7265	0.7120	0.6978	0.7714	0.7558	0.7403	0.8564	0.8388	0.8209
5	0.7278	0.7132	0.6991	0.7728	0.7571	0.7417	0.8581	0.8403	0.8226
7.5	0.7303	0.7160	0.7023	0.7757	0.7602	0.7452	0.8613	0.8439	0.8267
10	0.7324	0.7187	0.7053	0.7779	0.7632	0.7485	0.8641	0.8473	0.8305
12.5	0.7351	0.7213	0.7083	0.7808	0.7660	0.7517	0.8674	0.8506	0.8343
15	0.7374	0.7238	0.7110	0.7833	0.7688	0.7548	0.8703	0.8538	0.8379
17.5	0.7393	0.7263	0.7137	0.7854	0.7715	0.7578	0.8728	0.8569	0.8412
20	0.7418	0.7287	0.7163	0.7881	0.7741	0.7607	0.8759	0.8599	0.8446
22.5	0.7439	0.7311	0.7188	0.7904	0.7767	0.7634	0.8786	0.8629	0.8478
25	0.7456	0.7333	0.7212	0.7923	0.7791	0.7661	0.8809	0.8658	0.8509
		$x_1 = 0.2916$			$x_1 = 0.4000$			$x_1 = 0.4889$	
0.1	0.9426	0.9213	0.8989	1.0326	1.0089	0.9839	1.1025	1.0768	1.0498
1	0.9441	0.9229	0.9017	1.0343	1.0107	0.9870	1.1043	1.0788	1.0531
2	0.9458	0.9248	0.9038	1.0362	1.0129	0.9894	1.1065	1.0812	1.0558
3	0.9473	0.9266	0.9059	1.0380	1.0149	0.9918	1.1084	1.0835	1.0584
4	0.9487	0.9283	0.9079	1.0396	1.0169	0.9941	1.1102	1.0857	1.0609
5	0.9506	0.9301	0.9099	1.0417	1.0189	0.9963	1.1124	1.0878	1.0633
7.5	0.9543	0.9342	0.9147	1.0459	1.0237	1.0018	1.1170	1.0930	1.0693
10	0.9576	0.9383	0.9192	1.0497	1.0284	1.0070	1.1211	1.0980	1.0750
12.5	0.9614	0.9422	0.9235	1.0540	1.0327	1.0119	1.1257	1.1028	1.0804
15	0.9647	0.9459	0.9277	1.0578	1.0370	1.0166	1.1299	1.1074	1.0855
17.5	0.9677	0.9493	0.9317	1.0611	1.0410	1.0211	1.1335	1.1118	1.0904
20	0.9711	0.9530	0.9355	1.0649	1.0449	1.0254	1.1377	1.1162	1.0951
22.5	0.9742	0.9564	0.9392	1.0684	1.0489	1.0296	1.1414	1.1203	1.0996
25	0.9768	0.9596	0.9427	1.0715	1.0525	1.0336	1.1448	1.1243	1.1039
		$x_1 = 0.5911$			$x_1 = 0.7017$			$x_1 = 0.8039$	
0.1	1.1793	1.1519	1.1226	1.2580	1.2284	1.1971	1.3292	1.2972	1.2640
1	1.1813	1.1541	1.1261	1.2601	1.2307	1.2009	1.3308	1.2998	1.2679
2	1.1835	1.1567	1.1290	1.2626	1.2335	1.2040	1.3334	1.3027	1.2713
3	1.1857	1.1591	1.1319	1.2649	1.2361	1.2070	1.3359	1.3055	1.2745
4	1.1876	1.1615	1.1346	1.2670	1.2387	1.2099	1.3381	1.3082	1.2777
5	1.1900	1.1639	1.1373	1.2695	1.2413	1.2129	1.3408	1.3109	1.2807
7.5	1.1950	1.1695	1.1438	1.2749	1.2474	1.2198	1.3465	1.3174	1.2882
10	1.1995	1.1749	1.1499	1.2798	1.2532	1.2264	1.3517	1.3236	1.2951
12.5	1.2045	1.1801	1.1558	1.2851	1.2589	1.2327	1.3573	1.3295	1.3018
15	1.2090	1.1851	1.1613	1.2900	1.2642	1.2387	1.3624	1.3352	1.3081
17.5	1.2130	1.1899	1.1666	1.2943	1.2694	1.2445	1.3670	1.3407	1.3142
20	1.2175	1.1945	1.1717	1.2991	1.2744	1.2499	1.3721	1.3460	1.3200
22.5	1.2216	1.1991	1.1766	1.3035	1.2792	1.2552	1.3767	1.3511	1.3255
25	1.2252	1.2034	1.1813	1.3074	1.2838	1.2603	1.3809	1.3560	1.3309
		$x_1 = 0.9594$							
0.1	1.4316	1.3978	1.3623						
1	1.4339	1.4005	1.3663						
2	1.4367	1.4037	1.3699						
3	1.4393	1.4067	1.3734						
4	1.4417	1.4096	1.3767						
5	1.4445	1.4125	1.3800						
7.5	1.4506	1.4194	1.3879						
10	1.4561	1.4260	1.3954						
12.5	1.4621	1.4323	1.4025						
15	1.4675	1.4383	1.4092						
17.5	1.4725	1.4442	1.4157						
20	1.4779	1.4499	1.4219						
22.5	1.4827	1.4553	1.4278						
25	1.4872	1.4605	1.4335						

correct calibration over wide ranges of temperature and pressure and ensures an uncertainty in density determination lower than $10^{-4} \text{ g}\cdot\text{cm}^{-3}$. The measurement of density with this calibration implies making an extrapolation when determining the pure HFE (or rich HFE concentration mixtures) densities. The validity of this extrapolation technique for this particular experimental device was demonstrated previously,⁵ where the method proved to be correct for the studied density range through comparison of determined density values for tetrachloromethane with recommended literature values.

Results and Discussion

Pure ethyl nonfluorobutyl ether densities were determined using the described method. Pure *n*-hexane density values were taken from the cited previous work.⁸ Then, the values corresponding to their binary mixture in the whole composition range were measured for 10 different concentrations. Ethyl nonfluorobutyl ether density values were compared with those deter-

mined in a previous work,⁵ yielding an average absolute deviation (AAD) of $7\cdot 10^{-4} \text{ g}\cdot\text{cm}^{-3}$ and an APD of 0.05 %.

These parameters, AAD and APD, appearing throughout the text and tables, are defined as follows:

$$\text{AAD} = \frac{1}{N} \sum_{i=1}^N |\rho_{i-\text{exp}} - \rho_{i-\text{cal}}| \quad (1)$$

$$\text{APD} = \frac{100}{N} \sum_{i=1}^N \left| \frac{\rho_{i-\text{exp}} - \rho_{i-\text{cal}}}{\rho_{i-\text{exp}}} \right| \quad (2)$$

where *N* stands for the number of experimental data, and $\rho_{i-\text{exp}}$ and $\rho_{i-\text{cal}}$ are the experimental and correlated density, respectively.

Pure compound densities, and those corresponding to each mole fraction of the mixture, were correlated using a modified

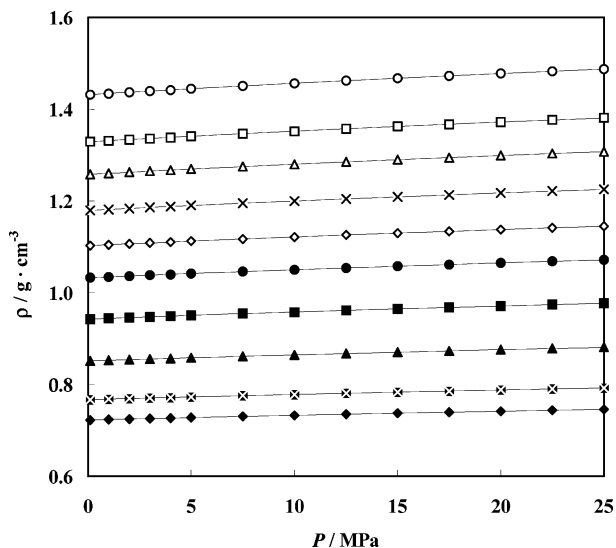


Figure 1. High-pressure experimental density ($\rho/\text{g}\cdot\text{cm}^{-3}$) for the mixture ethyl nonafluorobutyl ether + hexane at 283.15 K, for different mole fractions of HFE: \blacklozenge , 0.0532; white X, 0.0989; \blacktriangle , 0.1885; \blacksquare , 0.2916; \bullet , 0.4000; \diamond , 0.4889; \times , 0.5911; \triangle , 0.7017; \square , 0.8039; \circ , 0.9594; and —, Tait equation correlation.

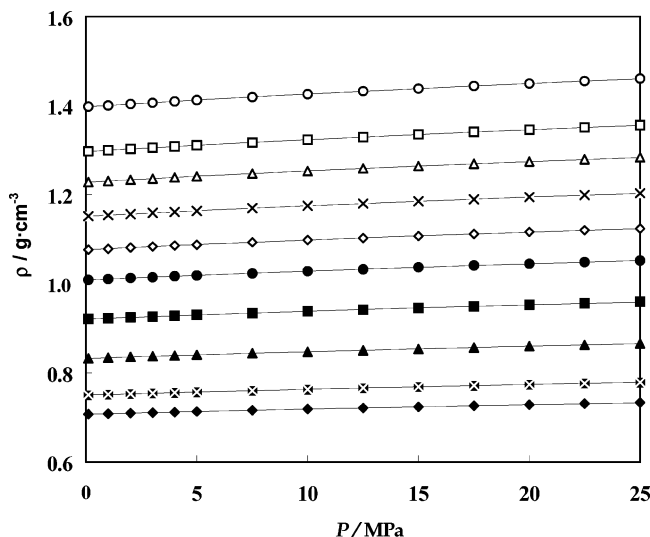


Figure 2. High-pressure experimental density ($\rho/\text{g}\cdot\text{cm}^{-3}$) for the mixture ethyl nonafluorobutyl ether + hexane at 298.15 K, for different mole fractions of HFE: \blacklozenge , 0.0532; white X, 0.0989; \blacktriangle , 0.1885; \blacksquare , 0.2916; \bullet , 0.4000; \diamond , 0.4889; \times , 0.5911; \triangle , 0.7017; \square , 0.8039; \circ , 0.9594; and —, Tait equation correlation.

Tait equation:

$$\rho(P, T) = \frac{\rho(P_0, T)}{1 - C \ln\left(\frac{B(T) + P}{B(T) + P_0}\right)} \quad (3)$$

where P_0 stands for the reference pressure (0.1 MPa). Reference pressure densities were fitted using a second-order temperature-dependent polynomial:

$$\rho(P_0, T) = \sum_{i=0}^2 \rho_{0i} T^i \quad (4)$$

where ρ_{0i} are the fitting parameters. In eq 3, C and $B(T)$ are fitted to high-pressure densities, the latter being a temperature-

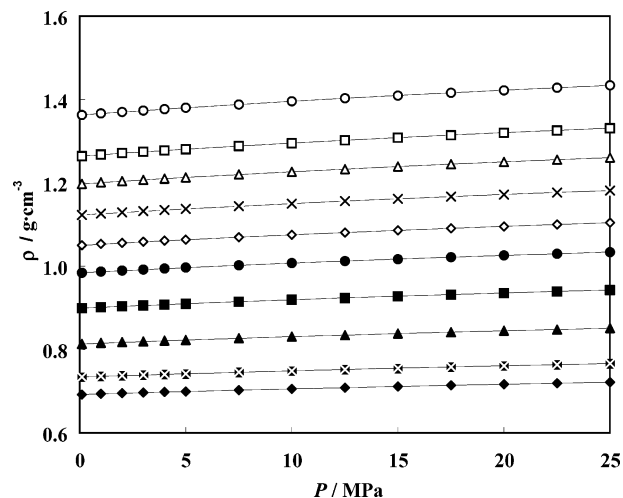


Figure 3. High-pressure experimental density ($\rho/\text{g}\cdot\text{cm}^{-3}$) for the mixture ethyl nonafluorobutyl ether + hexane at 313.15 K, for different mole fractions of HFE: \blacklozenge , 0.0532; white X, 0.0989; \blacktriangle , 0.1885; \blacksquare , 0.2916; \bullet , 0.4000; \diamond , 0.4889; \times , 0.5911; \triangle , 0.7017; \square , 0.8039; \circ , 0.9594; and —, Tait equation correlation.

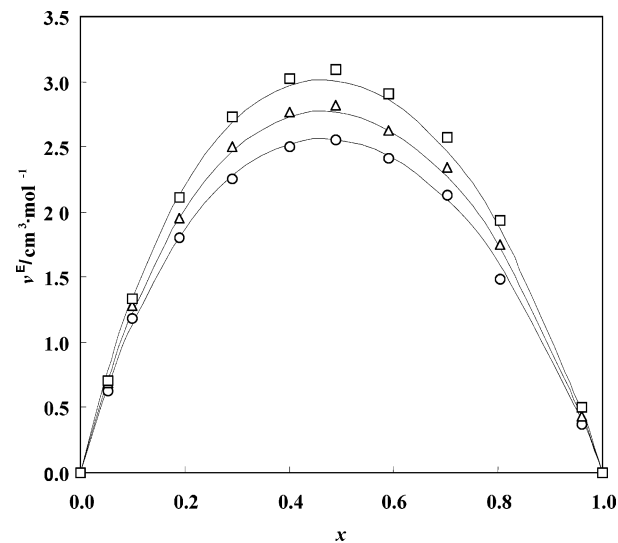


Figure 4. Excess molar volumes ($V^E/\text{cm}^3\cdot\text{mol}^{-1}$) of ethyl nonafluorobutyl ether + *n*-hexane at 0.1 MPa and \circ , 283.15 K; \triangle , 298.15 K; \square , 313.15 K; and —, modified Redlich–Kister correlation.

dependent expression:

$$B(T) = \sum_{i=0}^2 B_i T^i \quad (5)$$

where B_i are the fitting parameters. Experimental mixture density data are listed in Table 1. In Table 2, the Tait equation fitting coefficients are listed, together with the corresponding AAD and APD values. Mixture density values have been plotted against pressure in Figures 1, 2, and 3 at the temperatures of (283.15, 298.15, and 313.15) K, respectively.

From the measured density data, the excess molar volume (V^E) was calculated for the mixture. Due to the large number of experimental data, an attempt was made to correlate all excess molar volume data with a single modified Redlich–Kister equation, including a dependence on both pressure and temperature:

$$V^E = x(1-x)(1+AP) \left[1 + \sum_{i=1}^2 B_i T^i \right] \left[\sum_{j=0}^3 C_j (2x-1)^j \right] \quad (6)$$

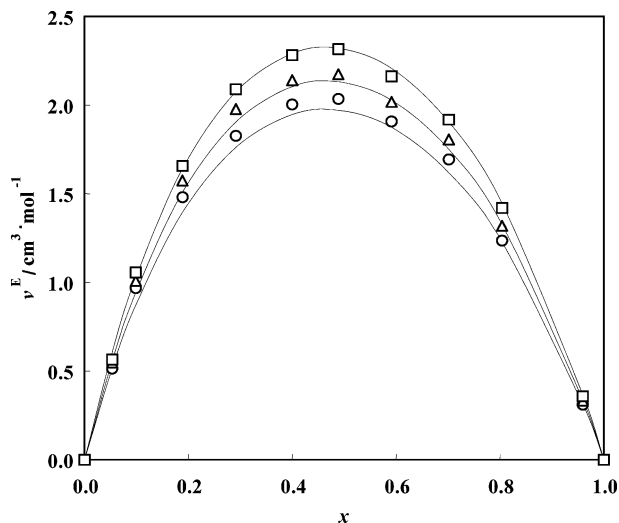


Figure 5. Excess molar volumes ($V^E/\text{cm}^3\cdot\text{mol}^{-1}$) of ethyl nonafluorobutyl ether + hexane at 25 MPa and \circ , 283.15 K; \triangle , 298.15 K; \square , 313.15 K; and $-$, modified Redlich–Kister correlation.

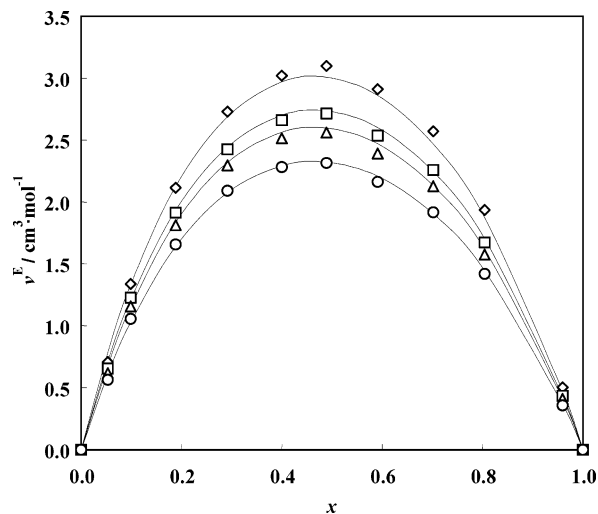


Figure 7. Excess molar volumes ($V^E/\text{cm}^3\cdot\text{mol}^{-1}$) of ethyl nonafluorobutyl ether + hexane at 313.15 K and \diamond , 0.1 MPa; \square , 10 MPa; \triangle , 15 MPa; \circ , 25 MPa; and $-$, modified Redlich–Kister correlation.

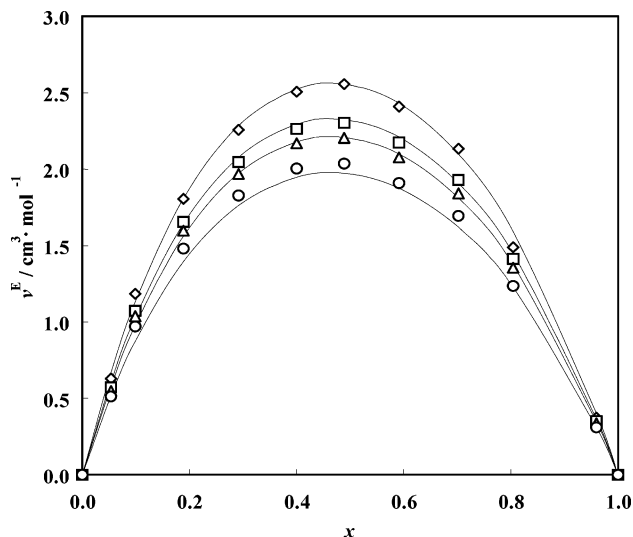


Figure 6. Excess molar volumes ($V^E/\text{cm}^3\cdot\text{mol}^{-1}$) of ethyl nonafluorobutyl ether + hexane at 283.15 K and \diamond , 0.1 MPa; \square , 10 MPa; \triangle , 15 MPa; \circ , 25 MPa; and $-$, modified Redlich–Kister correlation.

where x stands for the mole fraction, and A , B_i , and C_j are the fitting parameters. The maximum value of the i and j indices was determined in each case by applying the F -test due to Bevington.¹¹ This way, the correlation of the complete set of

V^E values was obtained with only seven parameters, listed in Table 3 together with the fitting deviations. The fact of using only one equation to fit the complete set of V^E data represents a remarkable economy in the number of parameters, and the deviations obtained were similar to those obtained by fitting V^E data at each temperature and pressure using the usual Redlich–Kister equation.⁷ As it could be expected for the values presented previously,⁷ again the computed V^E are positive and present very large values. This behavior had been already shown for other HFE + alkane mixtures by Minamihounoki et al.¹² The similarity with the trend observed for the volumetric behavior of perfluoroalkane + n -alkane binary mixtures¹³ must be emphasized. This similarity allows to think that for HFES, the perfluorinated chain determines the volumetric trend, and thus the discussions of solute–solvent interactions and packing and order effects for mixtures containing both types of compounds are very close to each other. In the case of HFES, the presence of the ether group could let think about the presence of self-association effects that would influence the mixing process. Regarding the effect of the ether group that links the perfluorinated and the aliphatic chain in the HFE molecule, in previous works^{5,7} it has been shown that the molecular structure and the large size of the perfluorinated methyl and methylene groups produce an effect of steric hindrance that reduces the effective possibility of contact for the ether group, which leads to a negligible influence of a possible presence of chemical associa-

Table 2. Modified Tait Equation Coefficients for Mixture Density Correlation, and Obtained Deviations, AAD/ $\text{g}\cdot\text{cm}^{-3}$ and APD/%

x_1	$\rho_{00}/\text{g}\cdot\text{cm}^{-3}$	$\rho_{01}/\text{g}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$	$\rho_{02}/\text{g}\cdot\text{cm}^{-3}\cdot\text{K}^{-2}$	C	B_0/MPa	$B_1/\text{MPa}\cdot\text{K}^{-1}$	$B_2/\text{MPa}\cdot\text{K}^{-2}$	AAAD/ $\text{g}\cdot\text{cm}^{-3}$	APD/%
0.0000	$8.6808\cdot 10^{-1}$	$-5.1148\cdot 10^{-4}$	$-6.8804\cdot 10^{-7}$	$7.3554\cdot 10^{-2}$	475.30	-2.4322	$3.2845\cdot 10^{-3}$	$1.4\cdot 10^{-4}$	$2.2\cdot 10^{-2}$
0.0532	$8.6950\cdot 10^{-1}$	$-6.2703\cdot 10^{-5}$	$-1.6133\cdot 10^{-6}$	$7.0154\cdot 10^{-2}$	-121.63	1.5131	$-3.2736\cdot 10^{-3}$	$1.5\cdot 10^{-4}$	$2.1\cdot 10^{-2}$
0.0989	$9.3895\cdot 10^{-1}$	$-1.5749\cdot 10^{-4}$	$-1.5911\cdot 10^{-6}$	$6.9997\cdot 10^{-2}$	12.996	$5.7695\cdot 10^{-1}$	$-1.6708\cdot 10^{-3}$	$1.6\cdot 10^{-4}$	$2.0\cdot 10^{-2}$
0.1885	$9.8820\cdot 10^{-1}$	$2.2800\cdot 10^{-4}$	$-2.5133\cdot 10^{-6}$	$7.3227\cdot 10^{-2}$	-62.529	1.0980	$-2.5652\cdot 10^{-3}$	$1.6\cdot 10^{-4}$	$1.9\cdot 10^{-2}$
0.2916	1.1560	$-1.1797\cdot 10^{-4}$	$-2.2444\cdot 10^{-6}$	$7.4657\cdot 10^{-2}$	-3.1204	$6.8352\cdot 10^{-1}$	$-1.8583\cdot 10^{-3}$	$1.6\cdot 10^{-4}$	$1.7\cdot 10^{-2}$
0.4000	1.2586	$-5.1685\cdot 10^{-5}$	$-2.6356\cdot 10^{-6}$	$7.6184\cdot 10^{-2}$	84.894	$8.1323\cdot 10^{-2}$	$-8.3792\cdot 10^{-4}$	$1.6\cdot 10^{-4}$	$1.5\cdot 10^{-2}$
0.4889	1.3348	$2.5216\cdot 10^{-5}$	$-2.9867\cdot 10^{-6}$	$7.6735\cdot 10^{-2}$	80.952	$1.0106\cdot 10^{-1}$	$-8.6579\cdot 10^{-4}$	$1.6\cdot 10^{-4}$	$1.5\cdot 10^{-2}$
0.5911	1.3382	$6.4119\cdot 10^{-4}$	$-4.2467\cdot 10^{-6}$	$7.7083\cdot 10^{-2}$	72.264	$1.5284\cdot 10^{-1}$	$-9.4603\cdot 10^{-4}$	$1.7\cdot 10^{-4}$	$1.5\cdot 10^{-2}$
0.7017	1.5211	$6.4450\cdot 10^{-5}$	$-3.5089\cdot 10^{-6}$	$7.8283\cdot 10^{-2}$	130.49	$-2.3684\cdot 10^{-1}$	$-2.9226\cdot 10^{-4}$	$1.5\cdot 10^{-4}$	$1.2\cdot 10^{-2}$
0.8039	1.7406	$-8.0168\cdot 10^{-4}$	$-2.3000\cdot 10^{-6}$	$7.9429\cdot 10^{-2}$	357.71	-1.7199	$2.1304\cdot 10^{-3}$	$2.3\cdot 10^{-4}$	$1.7\cdot 10^{-2}$
0.9594	1.7238	$1.2241\cdot 10^{-4}$	$-4.0778\cdot 10^{-6}$	$7.7483\cdot 10^{-2}$	167.15	$-4.8068\cdot 10^{-1}$	$1.1160\cdot 10^{-4}$	$1.6\cdot 10^{-4}$	$1.1\cdot 10^{-2}$
1.0000	1.9721	$-1.3710\cdot 10^{-3}$	$-1.5743\cdot 10^{-6}$	$8.0730\cdot 10^{-2}$	302.37	-1.3775	$1.6190\cdot 10^{-3}$	$9.7\cdot 10^{-5}$	$6.7\cdot 10^{-3}$

Table 3. Modified Redlich Kister Equation 6 Coefficients, for $V^E/\text{cm}^3\cdot\text{mol}^{-1}$ Correlation, and Obtained Deviations

A/MPa $^{-1}$	B_1/K^{-1}	B_2/K^{-2}	$C_0/\text{cm}^3\cdot\text{mol}^{-1}$	$C_1/\text{cm}^3\cdot\text{mol}^{-1}$	$C_2/\text{cm}^3\cdot\text{mol}^{-1}$	$C_3/\text{cm}^3\cdot\text{mol}^{-1}$	AAAD/ $\text{cm}^3\cdot\text{mol}^{-1}$	APD/%
$-9.1597\cdot 10^{-3}$	$-6.0909\cdot 10^{-3}$	$1.4741\cdot 10^{-5}$	22.327	-2.4771	4.2799	-1.3663	$2.8\cdot 10^{-2}$	2.2

tion in the fluid. This behavior is supported by the similarity of the computed internal pressure values for HFEs and perfluoroalkanes.

Figures 4 and 5 present the calculated V^E and the correlations obtained with eq 6 at (0.1 and 25) MPa. Figures 6 and 7 present a similar representation of V^E , in this case at constant temperatures (283.15 and 313.15) K and varying pressure in each case. The effect of pressure and temperature is clear on the volumetric behavior of the mixture, as V^E increases with the increasing temperature and presents the opposite trend with pressure, as it could be expected a priori from the influence of both magnitudes on molecular arrangement. In addition, and if compared with the values presented previously,⁵ the effect of increasing the chain length of the aliphatic chain in the segregated HFE (from methyl to ethyl) causes a reduction of the maximum absolute values of the calculated V^E , an effect that could be expected because, as stated before, the highly non-ideal volumetric behavior of the mixture is due to the presence of the perfluorinated functional groups.

Conclusions

This work presents new data on high-pressure volumetric behavior of binary mixtures of HFEs and linear alkanes. The density data were obtained in a wide pressure range, from atmospheric conditions up to 25 MPa, and at temperatures between 283.15 K and 313.15 K. These data are useful to obtain an adequate description of thermophysical behavior of mixtures containing HFEs applying either equations of state or group-contribution models. The mixture studied here exhibits very large positive V^E , approaching the volumetric behavior of other mixtures of HFEs or perfluoroalkanes with linear alkanes.

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