

High-Pressure Densities of the Binary Mixture Methyl Nonafluorobutyl Ether + Hexane

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Densities at high pressures for the binary mixture of methylnonafluorobutyl ether + hexane were measured, as well as those corresponding to both pure fluids, in a pressure range from (0.1 to 25) MPa and at temperatures of (283.15, 293.15, and 313.15) K. A vibrating tube densimeter connected to a high-pressure measuring cell was used for the density determination. Experimental data for the mixture were fitted using a modified Tait equation. From this set of experimental data, excess molar volumes of the mixture were calculated and then correlated using a temperature- and pressure-dependent modified Redlich–Kister equation.

1. Introduction

The continuous search for environmentally friendly halogenated fluids, which could be suitable to replace other compounds, proven to be harmful, in industrial applications, has lately attracted attention to hydrofluoroethers (HFEs).^{1,2} These compounds include an ether group and two partially fluorinated aliphatic chains. HFEs have been proposed to replace some chlorofluorocarbons (CFCs) and also hydrofluorocarbons (HFCs) in applications such as the cleaning of electronic compounds or low-temperature heat-exchange fluids.³ HFEs present a promising environmental profile, including zero ozone-depleting potential (ODP), low global warming potential (GWP), and short atmospheric lifetimes.⁴ Among these compounds, segregated HFEs (those including both an aliphatic and a perfluorinated chain) have been pointed out for their promising profile, but experimental thermophysical data are still scarce in the literature, so an adequate description of their thermodynamic behavior is not yet available. In previous works,^{5,6} experimental high-pressure densities and speeds of sound, respectively, have been reported for methyl and ethyl nonafluorobutyl ether, and a paper describing the volumetric behavior of pure segregated HFEs using PC-SAFT EOS has also been published.⁷ As a continuation of this work, in this paper the mixing behavior of methyl nonafluorobutyl ether is studied through its binary mixture with hexane. Thus, experimental ρ_{PT} values have been measured and correlated using a modified Tait equation, and the corresponding excess molar volumes have been calculated.

2. Experimental Section

Hexane was supplied by Fluka (mass purity >99.5%). Methylnonafluorobutyl ether was supplied by TCI (Tokyo Chemicals Industries, Japan) with a purity of 99.8%. This fluid is actually a mixture of two inseparable structural isomers, with the same physical properties, containing 39.1% methyl nonafluorobutyl ether ($\text{CF}_3(\text{CF}_2)_3\text{OCH}_3$, CAS

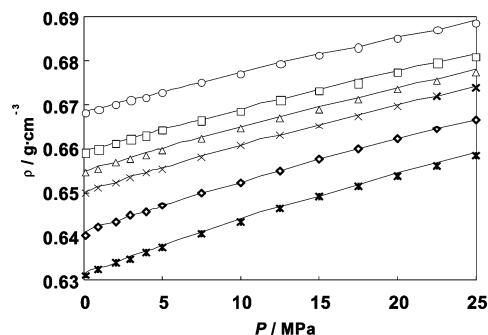


Figure 1. High-pressure experimental density ($\rho/\text{g}\cdot\text{cm}^{-3}$) of hexane at 283.15 K (\circ), 293.15 K (\square), 298.15 K (\triangle), 303.15 K (\times), 313.15 K (\diamond), and 323.15 K ($*$) plotted against the literature recommended correlation (Cibulka,¹² solid line).

no. 163702-07-6) and 60.7% methyl nonafluoroisobutyl ether ($(\text{CF}_3)_2\text{CFCF}_2\text{OCH}_3$, CAS no. 163702-08-7). Both liquids were degassed in an ultrasound bath, stored over molecular sieves to remove traces of moisture, and kept in an 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, connected to an external Anton Paar 512 P high-pressure measuring cell, that enables density measurements up to 70 MPa. The measuring principle consists of the determination of the vibration period of a U-shaped cell containing the fluid sample. Temperature stability is maintained through a PolyScience 9510 circulating fluid thermostatic bath, and the temperature is measured using a CKT-100 platinum probe placed beside the measuring cell, which ensures an uncertainty that has been estimated to be lower than 5×10^{-2} K. Pressure is generated and controlled using a Ruska 7610 pressure controller, which ensures a pressure stability of 2×10^{-3} MPa, and the hydraulic fluid (oil) is separated from the sample using a Teflon membrane separator provided by Pressurements. The right pressure transmission through the separator membrane is ensured by measuring the sample pressure with an SI digital manometer, with an uncertainty of 10^{-2} MPa. Mixture samples were prepared by weight using an AND HM 202

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Table 1. Experimental Densities (ρ) for the Mixture (x)Methylnonafluorobutyl Ether + (1 - x)Hexane

P/MPa	$\rho/\text{g}\cdot\text{cm}^{-3}$								
	283.15 K	298.15 K	313.15 K	283.15 K	298.15 K	313.15 K	283.15 K	298.15 K	313.15 K
		$x = 0.0469$			$x = 0.0867$			$x = 0.1508$	
0.1	0.7151	0.7001	0.6845	0.7545	0.7384	0.7215	0.8177	0.7997	0.7808
1	0.7161	0.7012	0.6866	0.7555	0.7396	0.7238	0.8189	0.8010	0.7833
2	0.7172	0.7024	0.6879	0.7567	0.7409	0.7252	0.8202	0.8026	0.7850
3	0.7183	0.7036	0.6893	0.7579	0.7422	0.7267	0.8216	0.8041	0.7867
4	0.7191	0.7047	0.6906	0.7588	0.7435	0.7281	0.8227	0.8055	0.7883
5	0.7204	0.7058	0.6918	0.7603	0.7448	0.7295	0.8242	0.8070	0.7899
7.5	0.7229	0.7086	0.6950	0.7629	0.7478	0.7330	0.8274	0.8104	0.7939
10	0.7250	0.7113	0.6980	0.7653	0.7507	0.7362	0.8299	0.8137	0.7975
12.5	0.7275	0.7138	0.7008	0.7681	0.7534	0.7393	0.8331	0.8169	0.8011
15	0.7298	0.7163	0.7037	0.7705	0.7560	0.7424	0.8359	0.8200	0.8045
17.5	0.7317	0.7188	0.7063	0.7726	0.7589	0.7453	0.8383	0.8230	0.8078
20	0.7341	0.7212	0.7089	0.7752	0.7613	0.7481	0.8412	0.8258	0.8110
22.5	0.7362	0.7236	0.7113	0.7775	0.7639	0.7508	0.8437	0.8287	0.8141
25	0.7380	0.7257	0.7138	0.7794	0.7662	0.7534	0.8459	0.8314	0.8170
		$x = 0.2414$			$x = 0.3201$			$x = 0.3895$	
0.1	0.9034	0.8827	0.8610	0.9763	0.9534	0.9294	1.0389	1.0139	0.9878
1	0.9048	0.8843	0.8638	0.9780	0.9552	0.9323	1.0406	1.0158	0.9909
2	0.9064	0.8862	0.8659	0.9797	0.9573	0.9346	1.0425	1.0182	0.9934
3	0.9080	0.8878	0.8678	0.9815	0.9592	0.9368	1.0445	1.0202	0.9959
4	0.9092	0.8895	0.8698	0.9829	0.9611	0.9391	1.0461	1.0224	0.9983
5	0.9110	0.8911	0.8717	0.9849	0.9630	0.9411	1.0482	1.0244	1.0007
7.5	0.9146	0.8951	0.8762	0.9889	0.9675	0.9463	1.0526	1.0293	1.0064
10	0.9177	0.8990	0.8805	0.9925	0.9718	0.9512	1.0565	1.0340	1.0117
12.5	0.9213	0.9028	0.8850	0.9965	0.9760	0.9559	1.0608	1.0386	1.0168
15	0.9245	0.9063	0.8887	1.0001	0.9800	0.9604	1.0647	1.0430	1.0217
17.5	0.9273	0.9098	0.8925	1.0032	0.9838	0.9647	1.0682	1.0472	1.0264
20	0.9306	0.9132	0.8962	1.0069	0.9876	0.9687	1.0721	1.0512	1.0308
22.5	0.9336	0.9163	0.8997	1.0102	0.9912	0.9727	1.0757	1.0552	1.0351
25	0.9361	0.9195	0.9031	1.0131	0.9946	0.9764	1.0788	1.0590	1.0393
		$x = 0.4928$			$x = 0.6137$			$x = 0.6937$	
0.1	1.1304	1.1026	1.0734	1.2340	1.2032	1.1706	1.3015	1.2688	1.2342
1	1.1323	1.1047	1.0769	1.2361	1.2057	1.1744	1.3038	1.2715	1.2382
2	1.1345	1.1073	1.0797	1.2386	1.2085	1.1777	1.3064	1.2745	1.2417
3	1.1366	1.1097	1.0825	1.2409	1.2112	1.1808	1.3089	1.2773	1.2450
4	1.1384	1.1121	1.0852	1.2430	1.2138	1.1839	1.3111	1.2802	1.2482
5	1.1407	1.1144	1.0879	1.2456	1.2164	1.1869	1.3139	1.2829	1.2514
7.5	1.1457	1.1199	1.0943	1.2511	1.2226	1.1941	1.3196	1.2895	1.2590
10	1.1501	1.1252	1.1003	1.2560	1.2285	1.2007	1.3249	1.2958	1.2661
12.5	1.1549	1.1303	1.1060	1.2613	1.2342	1.2072	1.3305	1.3018	1.2730
15	1.1593	1.1352	1.1115	1.2662	1.2395	1.2132	1.3357	1.3076	1.2795
17.5	1.1632	1.1398	1.1167	1.2705	1.2448	1.2190	1.3403	1.3131	1.2856
20	1.1675	1.1444	1.1217	1.2753	1.2498	1.2246	1.3454	1.3185	1.2915
22.5	1.1716	1.1489	1.1265	1.2797	1.2547	1.2299	1.3500	1.3236	1.2972
25	1.1751	1.1530	1.1311	1.2837	1.2593	1.2350	1.3542	1.3285	1.3026
		$x = 0.7915$			$x = 0.8959$			$x = 0.9490$	
0.1	1.3832	1.3484	1.3119	1.4694	1.4322	1.3931	1.5137	1.4754	1.4351
1	1.3856	1.3512	1.3155	1.4718	1.4352	1.3975	1.5161	1.4783	1.4395
2	1.3883	1.3544	1.3192	1.4747	1.4386	1.4013	1.5190	1.4818	1.4433
3	1.3910	1.3574	1.3228	1.4775	1.4417	1.4050	1.5219	1.4851	1.4472
4	1.3934	1.3604	1.3263	1.4800	1.4449	1.4087	1.5245	1.4883	1.4509
5	1.3962	1.3633	1.3296	1.4830	1.4480	1.4123	1.5275	1.4915	1.4545
7.5	1.4023	1.3703	1.3377	1.4896	1.4553	1.4207	1.5341	1.4989	1.4632
10	1.4079	1.3769	1.3453	1.4954	1.4624	1.4287	1.5400	1.5061	1.4714
12.5	1.4138	1.3834	1.3526	1.5016	1.4691	1.4363	1.5464	1.5130	1.4791
15	1.4193	1.3895	1.3595	1.5073	1.4755	1.4436	1.5523	1.5195	1.4865
17.5	1.4242	1.3953	1.3660	1.5124	1.4817	1.4505	1.5576	1.5258	1.4936
20	1.4296	1.4010	1.3722	1.5181	1.4876	1.4571	1.5633	1.5319	1.5004
22.5	1.4345	1.4064	1.3782	1.5232	1.4934	1.4634	1.5686	1.5378	1.5068
25	1.4390	1.4116	1.3840	1.5280	1.4989	1.4695	1.5734	1.5434	1.5131

balance with an accuracy of 10^{-4} g, which gives through propagation calculation an estimated uncertainty of 10^{-4} in the mole fraction determination.

The experimental technique has been described in detail,^{5,8} as well as the calibration used in this case that applies the method proposed by Lagourette et al.⁹ using water (density data obtained from Kell and Whalley¹⁰) and vacuum as calibrating fluids. This method enables us to obtaining the correct calibration over wide ranges of temperature and pressure and ensures an uncertainty in the density determination of less than 10^{-4} $\text{g}\cdot\text{cm}^{-3}$. To check the validity of the densimeter calibration, the density was determined for pure hexane in the pressure range from (0.1 to 25) MPa at temperatures from (283.15 to 323.15)

K. The measured values were compared with the correlations provided by Cibulka¹¹ and Cibulka and Hnědkovský.¹² The AAD (average absolute deviation) and APD (average percent deviation) values, listed in the Tables, are defined as follows:

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

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

where N stands for the number of experimental data and

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

x	ρ_{00}	ρ_{01}	ρ_{02}	C	b_0	b_1	b_2	AAD	APD
	$\text{g}\cdot\text{cm}^{-3}$	$\text{g}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$	$\text{g}\cdot\text{cm}^{-3}\cdot\text{K}^{-2}$		MPa	$\text{MPa}\cdot\text{K}^{-1}$	$\text{MPa}\cdot\text{K}^{-2}$	$\text{g}\cdot\text{cm}^{-3}$	%
0.0000	8.6808×10^{-1}	-5.1148×10^{-4}	-6.8804×10^{-7}	7.3554×10^{-2}	475.30	-2.4322	3.2845×10^{-3}	1.5×10^{-4}	2.2×10^{-2}
0.0469	8.7243×10^{-1}	-1.3467×10^{-4}	-1.4867×10^{-6}	6.9660×10^{-2}	-62.270	1.1260	-2.6460×10^{-3}	1.6×10^{-4}	2.3×10^{-2}
0.0867	8.9812×10^{-1}	2.6919×10^{-5}	-1.8867×10^{-6}	7.0673×10^{-2}	-92.530	1.3102	-2.9317×10^{-3}	1.6×10^{-4}	2.2×10^{-2}
0.1508	9.9809×10^{-1}	-1.0025×10^{-4}	-1.8956×10^{-6}	7.3666×10^{-2}	70.004	2.2578×10^{-1}	-1.1285×10^{-3}	1.6×10^{-4}	2.1×10^{-2}
0.2414	1.1027	-6.1228×10^{-5}	-2.2689×10^{-6}	7.3531×10^{-2}	39.375	4.0249×10^{-1}	-1.4014×10^{-3}	1.8×10^{-4}	2.1×10^{-2}
0.3201	1.1872	-2.2356×10^{-6}	-2.6222×10^{-6}	7.5403×10^{-2}	54.596	2.8193×10^{-1}	-1.1750×10^{-3}	1.5×10^{-4}	1.5×10^{-2}
0.3895	1.2887	-1.3901×10^{-4}	-2.6244×10^{-6}	7.7247×10^{-2}	119.41	-1.4469×10^{-1}	-4.7473×10^{-4}	1.6×10^{-4}	1.5×10^{-2}
0.4928	1.3817	2.7378×10^{-5}	-3.2311×10^{-6}	7.7577×10^{-2}	114.54	-1.2634×10^{-1}	-4.9322×10^{-4}	1.6×10^{-4}	1.5×10^{-2}
0.6139	1.4794	2.5899×10^{-4}	-3.9756×10^{-6}	7.7272×10^{-2}	126.56	-2.1773×10^{-1}	-3.3314×10^{-4}	1.6×10^{-4}	1.3×10^{-2}
0.6937	1.5427	4.0399×10^{-4}	-4.4356×10^{-6}	7.7980×10^{-2}	163.08	-4.6285×10^{-1}	7.8197×10^{-5}	1.5×10^{-4}	1.4×10^{-2}
0.7915	1.6976	3.3585×10^{-5}	-4.0400×10^{-6}	8.1134×10^{-2}	240.04	-9.5343×10^{-1}	8.7767×10^{-4}	8.6×10^{-5}	6.3×10^{-3}
0.8959	1.7977	9.2771×10^{-5}	-4.4222×10^{-6}	7.7897×10^{-2}	247.71	-1.0107	9.6798×10^{-4}	1.6×10^{-4}	1.1×10^{-2}
0.9490	1.8659	1.4282×10^{-6}	-4.3978×10^{-6}	7.8390×10^{-2}	265.44	-1.1177	1.1341×10^{-3}	1.5×10^{-4}	1.0×10^{-2}
1.0000	2.0429	-8.8362×10^{-4}	-2.9663×10^{-6}	8.0337×10^{-2}	350.21	-1.6803	2.0838×10^{-3}	8.8×10^{-5}	5.7×10^{-3}

Table 3. Modified Redlich–Kister Data (Equation 4) for V^E Correlation and Obtained Deviations

A	B_1	B_2	C_0	C_1	C_2	C_3	AAD	APD
MPa^{-1}	K^{-1}	K^{-2}	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$	%
-9.9346×10^{-3}	8.4093×10^{-3}	1.0917×10^{-4}	9.9978×10^{-1}	-1.2173×10^{-1}	1.6396×10^{-1}	-1.9751×10^{-1}	3.9×10^{-2}	2.6

the subscripts exptl and calcd refer to experimental and fitted values, respectively.

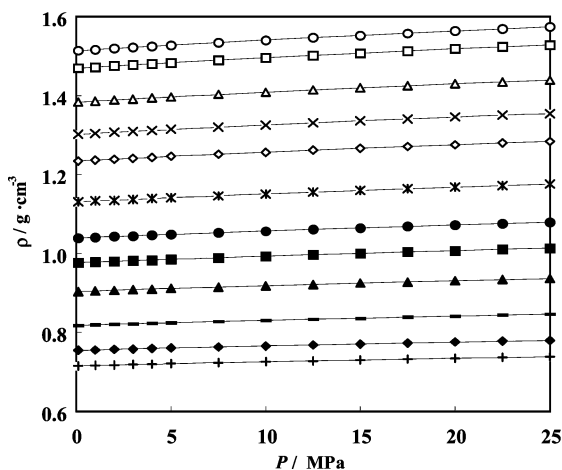


Figure 2. High-pressure experimental density ($\rho/\text{g}\cdot\text{cm}^{-3}$) for the mixture (x)methylnonafluorobutyl ether + ($1-x$)hexane at 283.15 K for different mole fractions of HFE [+ , 0.0469; \blacklozenge , 0.0867; - -, 0.1508; \blacktriangle , 0.2414; \blacksquare , 0.3201; \bullet , 0.3895; * , 0.4928; \diamond , 0.6139; \times , 0.6937; \triangle , 0.7915; \square , 0.8959; \circ , 0.9490] and the Tait equation correlation (solid line).

Results are plotted in Figure 1, and the determined densities present an average percent deviation (APD) of $4.5 \times 10^{-2}\%$ if compared with the correlation provided in the cited reference.¹² The root-mean-square deviation (rmsd, $\text{g}\cdot\text{cm}^{-3}$) of the determined density values of hexane if compared with the recommended high-pressure correlation is 3.4×10^{-4} , whereas the rmsd value provided by the authors for their correlation is 6.9×10^{-4} . Another factor to be taken into account when dealing with HFES, using, as has been described in this case, water as the calibrating fluid, is that an extrapolation in the described densimeter calibration is necessary in order to calculate density. In a previous work,⁵ it has been shown that this extrapolation is correct for the studied density range through a comparison of determined density values for tetrachloromethane with recommended literature values.

3. Results and Discussion

Pure methyl nonafluorobutyl ether and hexane densities were determined using the described method, as well as

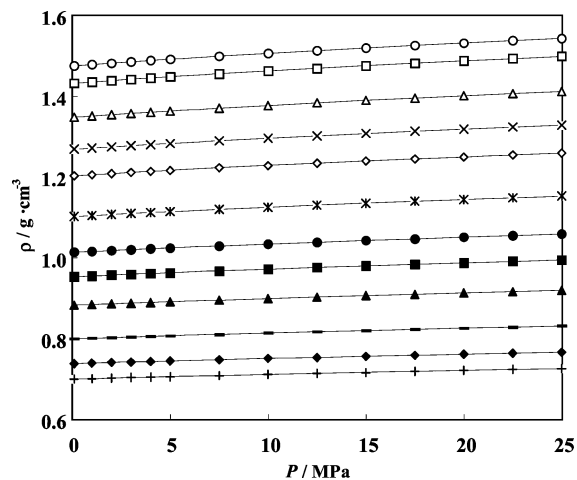


Figure 3. High-pressure experimental density ($\rho/\text{g}\cdot\text{cm}^{-3}$) for the mixture (x)methylnonafluorobutyl ether + ($1-x$)hexane at 298.15 K for different mole fractions of HFE [+ , 0.0469; \blacklozenge , 0.0867; - -, 0.1508; \blacktriangle , 0.2414; \blacksquare , 0.3201; \bullet , 0.3895; * , 0.4928; \diamond , 0.6139; \times , 0.6937; \triangle , 0.7915; \square , 0.8959; \circ , 0.9490] and the Tait equation correlation (solid line).

the values corresponding to their binary mixture over the whole composition range. Methylnonafluorobutyl ether density values were compared with those determined in previous work,⁵ yielding an AAD of $3.3 \times 10^{-4} \text{g}\cdot\text{cm}^{-3}$ and an APD of $2.1 \times 10^{-2}\%$. Pure compound densities and those corresponding to each mole fraction of the mixture were correlated using a modified 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 fit 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 fit to high-pressure densities, the latter being a

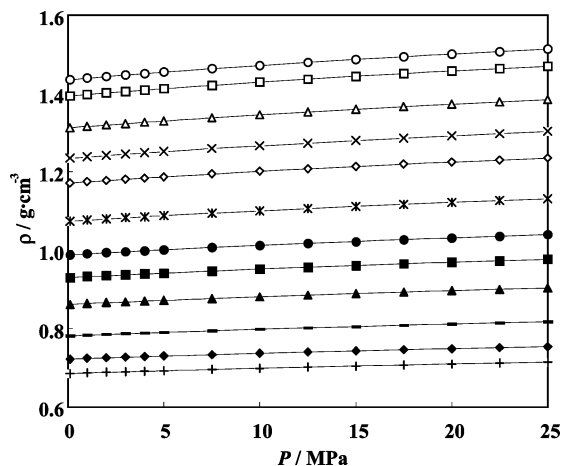


Figure 4. High-pressure experimental density ($\rho/\text{g}\cdot\text{cm}^{-3}$) for the mixture (x)methylnonafluorobutyl ether + $(1-x)$ hexane at 313.15 K for different mole fractions of HFE [$+$, 0.0469; \blacklozenge , 0.0867; $-$, 0.1508; \blacktriangle , 0.2414; \blacksquare , 0.3201; \bullet , 0.3895; $*$, 0.4928; \diamond , 0.6139; \times , 0.6937; \triangle , 0.7915; \square , 0.8959; \circ , 0.9490] and the Tait equation correlation (solid line).

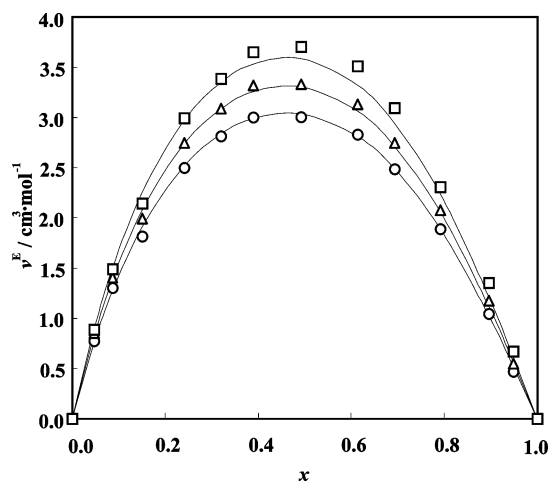


Figure 5. Excess molar volumes ($V^E/\text{cm}^3\cdot\text{mol}^{-1}$) of (x)methylnonafluorobutyl ether + $(1-x)$ hexane at 0.1 MPa and 283.15 K (\circ), 298.15 K (\triangle), and 313.15 K (\square) and the modified Redlich-Kister correlation (solid line).

temperature-dependent expression through the B_i parameters:

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

Experimental mixture density data are listed in Table 1. In Table 2, the Tait equation fitting coefficients are listed, together with the corresponding values of AAD and APD. Mixtures density values have been plotted against pressure in Figures 2, 3, and 4 at 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. A propagation error calculation of the accuracies in temperature and pressure determination and the uncertainty in density calculation yield an estimated uncertainty for the excess molar volume values of around $10^{-2} \text{ g}\cdot\text{cm}^{-3}$. Because of 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

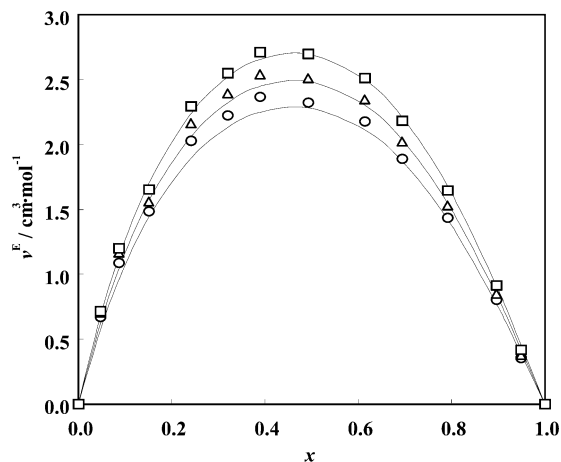


Figure 6. Excess molar volumes ($V^E/\text{cm}^3\cdot\text{mol}^{-1}$) of (x)methylnonafluorobutyl ether + $(1-x)$ hexane at 25 MPa and 283.15 K (\circ), 298.15 K (\triangle), and 313.15 K (\square) and the modified Redlich-Kister correlation (solid line).

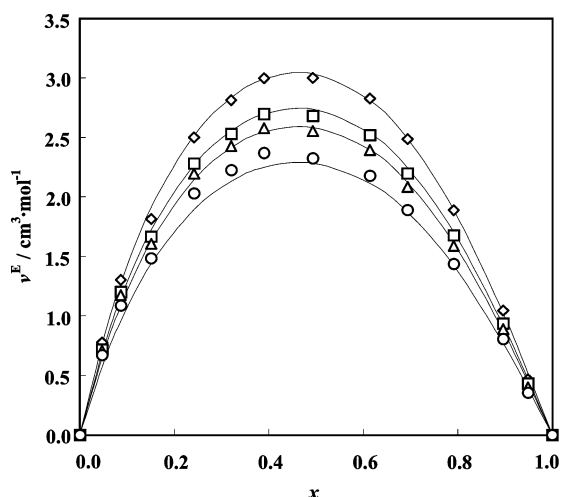


Figure 7. Excess molar volumes ($V^E/\text{cm}^3\cdot\text{mol}^{-1}$) of (x)methylnonafluorobutyl ether + $(1-x)$ hexane at 283.15 K and 0.1 MPa (\diamond), 10 MPa (\square), 15 MPa (\triangle), and 25 MPa (\circ) and the modified Redlich-Kister correlation (solid line).

on both pressure and temperature:

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

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.¹³ In 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. 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. The magnitude of the obtained V^E data must be emphasized because this mixture exhibits an unusually high departure from ideal volumetric behavior. The same trend at atmospheric pressure has been reported for the mixture of methyl nonafluorobutyl ether with n -pentane, n -heptane, and n -nonane by Minamihounoki et al.¹⁴ In another paper, Lepori et al.¹⁵ studied the volumetric behavior of perfluoroalkane + n -alkane binary mixtures, finding the same

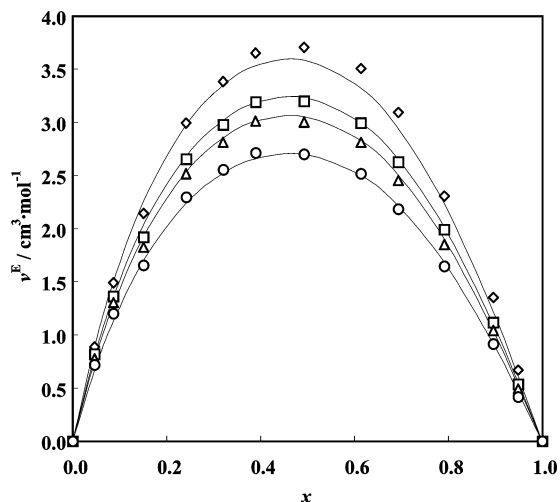


Figure 8. Excess molar volumes ($V^E/\text{cm}^3\cdot\text{mol}^{-1}$) of (x)methyl-nonafluorobutyl ether + ($1 - x$)hexane at 313.15 K and 0.1 MPa (\diamond), 10 MPa (\square), 15 MPa (\triangle), and 25 MPa (\circ) and the modified Redlich–Kister correlation (solid line).

behavior for V^E as the one exhibited by this HFE + n -alkane mixture. This similarity shows that in the case of this HFE it is the perfluorinated chain (much larger than the aliphatic chain) that determines to a great extent the volumetric trend, and thus the discussion of solute–solvent interactions and packing and order effects for mixtures containing perfluoroalkanes is closely related to the behavior of the mixture studied here. In the case of HFES, the presence of the ether group makes us think about the presence of self-association effects that would influence the mixing process. Nevertheless, the calculated values of internal pressure for methyl nonafluorobutyl ether⁵ present the trend of a nonstructured or nonassociated fluid (Barton¹⁶), and its value and variation are very close to those of perfluoroalkanes, so the potential effect of association in this case can be neglected, most probably because of the steric hindrance of the ether group (i.e., the low contact probability between ether groups caused by the HFE molecular structure). Figures 5 and 6 present the calculated V^E and the correlations obtained with eq 6 at (0.1 and 25) MPa. Figures 7 and 8 present a similar representation of V^E , in this case at constant temperatures of (283.15 and 313.15) K, and varying pressure in each case. The effect of pressure and temperature on the volumetric behavior of the mixture is clear because V^E increases with increasing temperature and presents the opposite trend with pressure, as could be expected a priori from the influence of both magnitudes on the molecular arrangement.

4. Conclusions

In this paper, our previous studies on the thermophysical properties of HFES are continued with the study of the influence of temperature on the volumetric behavior of the mixture methyl nonafluorobutyl ether + hexane. These data are useful in obtaining an adequate description of the thermophysical properties of mixtures containing HFES

applying either equations of state or group contribution models. The mixture studied exhibits a very large positive V^E , approaching the volumetric behavior of other mixtures of HFES or perfluoroalkanes with linear alkanes.

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