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PρTx Measurements for (1,1,1,2-Tetrafluoroethane + Triethylene Glycol Dimethyl Ether) at High Haloalkane Content

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Densities in the liquid phase were measured for (1,1,1,2-tetrafluoroethane + triethylene glycol dimethyl ether) using a vibrating-tube densimeter. Three mixtures with a molar fraction of refrigerant of 0.9485, 0.9655, and 0.9798 have been considered at temperatures from (283 to 323 K) at pressures up to 6 MPa. Such ranges are approximately those of interest for a compression refrigeration plant. The data at each composition were correlated with a Tait equation, and the excess volumes were also provided.

1. Introduction

The refrigerant 1,1,1,2-tetrafluoroethane (R134a) has become one of the main alternative to chlorofluorocarbon (CFC) refrigerants because of its better environmental characteristics, the thermodynamic performances in compression plants, and the compatibility with the existing refrigeration plants. Replacing CFCs with R134a also requires the choice of lubricants that are compatible and soluble with it. In fact, the mineral oils that were used with CFCs show low solubility in hydrofluorocarbon refrigerants.

The polyalkylene glycols (PAGs) have been proposed as suitable lubricants for R134a. The choice of the lubricant and the technical applications, as for instance the design of a refrigeration plant, require the knowledge of the thermophysical properties of the (refrigerant + lubricant) in order to choose the most effective one for the particular application. Different researchers have focused their attention on (R134a + PAGs), and for these systems measurements of solubility,[1−4] density,[5] and viscosity[6] have been published in the literature.

In the present work, the densities of (R134a + triethylene glycol dimethyl ether) (triethylene glycol dimethyl ether will be referred to herein after as TriEGDME) have been measured in the composition range that is usually encountered in refrigeration plant (i.e., for a lubricant mass content of less than 10 %).

2. Experimental Section

2.1. Materials. The fluid R134a ($CF_3{-}CH_2F$, $M = 102.03$ kg·kmol^{-1}, Chemical Abstracts Service Registry Number (CASRN) 811-97-2) was supplied by Solvay Fluor GmbH (Germany) with a stated purity of 99.9 mass %. TriEGDME ($CH_3O{-}(CH_2{-}CH_2{-}O)_3{-}CH_3$, $M = 178.23$ kg·kmol^{-1}, CASRN 112-49-2) was obtained from Acros Organics. For it a purity of 99.95 mass % and a water content of 0.017 mass % were verified by gas chromatography and Karl Fischer titration, respectively.

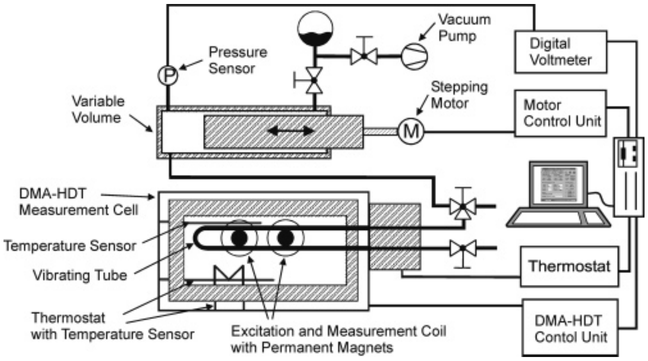

Figure 1. Schematic diagram of the computer-controlled density measurement unit.

2.2. Experimental Technique. 2.2.1. Apparatus. A computer-operated vibrating-tube densimeter designed for operation at temperatures from (273 to 623) K and pressures up to 40 MPa was used for the density measurements.

A schematic diagram of the densimeter apparatus is shown in Figure 1. The apparatus, the calibration, and the measurement procedure have been formerly described in detail by Ihmels and Gmehling.[7,8] A prototype of a high-pressure high-temperature vibrating-tube densimeter (DMA-HDT, Hastelloy C-276, Stabinger, Austria) is the essential part of the experimental setup. The temperature is measured using a nominally 100 Ω platinum resistance thermometer (calibrated on ITS-90), and the pressure is determined with a calibrated pressure sensor (model PDCR 921, pressure range 60 MPa, Druck, UK). The density values are obtained from the oscillation periods of the vibrating tube.

The uncertainty in temperature measurements is estimated to be ± 0.03 K, and the measurement of pressure has an estimated uncertainty of ± 6 kPa (calibrated with a dead weight balance). Considering the uncertainties of the variables and the accuracy of the densimeter, the density measurements have a maximum uncertainty of ± 0.3 kg·m^{-3}. The repeatability of the density measurements is about ± 0.05 kg·m^{-3}.

Using this apparatus, a large number of data points can be obtained in a rather short time with a minimum of manual effort. A temperature and pressure program is used to obtain a complete $p\rho T$ field for the desired component or mixture at fixed

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Table 1. Experimental Density Values *ρ* for (R134a + TriEGDME) in Dependence on Temperature *T*, Pressure *p*, and R134a Mole Fraction *x*

x	T/K	p/MPa	ρ/kg·m^{-3}	T/K	p/MPa	ρ/kg·m^{-3}	T/K	p/MPa	ρ/kg·m^{-3}
0.9485	283.27	1.086	1245.33	293.30	5.000	1230.18	313.35	2.990	1160.47
	283.27	2.000	1248.44	293.30	6.018	1233.75	313.35	3.990	1165.56
	283.27	3.016	1251.83	303.33	1.189	1184.28	313.35	4.985	1170.41
	283.27	4.003	1255.03	303.33	1.998	1188.03	313.35	5.997	1175.14
	283.27	5.009	1258.22	303.33	2.990	1192.49	323.39	1.737	1118.26
	283.27	6.019	1261.33	303.33	3.984	1196.79	323.39	1.994	1119.99
	293.30	1.086	1215.38	303.33	5.011	1201.05	323.39	3.007	1126.53
	293.30	2.016	1219.06	303.33	5.992	1205.02	323.39	3.987	1132.49
	293.30	2.998	1222.84	313.35	1.434	1152.06	323.39	4.990	1138.29
	293.30	3.985	1226.51	313.35	2.014	1155.26	323.39	5.982	1143.72
0.9655	283.29	1.047	1251.56	293.32	5.001	1236.10	313.36	3.010	1161.91
	283.29	1.992	1255.06	293.32	5.994	1239.88	313.37	4.000	1167.49
	283.29	2.996	1258.69	303.35	1.189	1186.88	313.37	5.010	1172.90
	283.29	3.988	1262.16	303.35	2.013	1191.11	313.37	5.984	1177.91
	283.29	4.999	1265.62	303.35	2.992	1195.95	323.41	1.737	1116.04
	283.29	5.987	1268.91	303.35	4.008	1200.76	323.41	1.998	1118.03
	293.32	1.047	1219.81	303.35	4.992	1205.25	323.41	3.002	1125.33
	293.32	2.002	1223.94	303.35	5.987	1209.62	323.41	4.001	1132.15
	293.32	2.997	1228.11	313.36	1.436	1152.44	323.41	4.985	1138.48
	293.32	3.984	1232.11	313.37	2.008	1155.97	323.41	6.012	1144.72
0.9798	283.28	1.070	1255.94	293.31	4.992	1239.84	313.35	2.982	1161.59
	283.28	1.986	1259.56	293.31	6.009	1243.96	313.36	3.986	1167.71
	283.28	2.984	1263.39	303.33	1.176	1187.73	313.35	4.986	1173.51
	283.28	4.004	1267.20	303.34	2.006	1192.33	313.36	5.983	1179.03
	283.28	4.996	1270.80	303.34	3.006	1197.65	323.39	1.731	1112.96
	283.28	5.989	1274.30	303.34	4.000	1202.73	323.39	1.989	1115.09
	293.31	1.086	1222.61	303.34	4.990	1207.56	323.40	3.001	1123.14
	293.31	2.003	1226.87	303.34	6.008	1212.35	323.40	4.006	1130.60
	293.31	2.985	1231.29	313.35	1.434	1151.46	323.40	4.997	1137.51
	293.31	4.010	1235.72	313.35	2.004	1155.29	323.40	5.982	1144.00

composition. The measurement system has been discussed in the Ph.D. dissertation of Ihmels.[9] Some more details for the calibration procedure and further applications of the apparatus (e.g., for supercritical measurements), were recently presented by Ihmels et al.[10]

2.2.2. Mixture Preparation. In the present work, three mixtures at various compositions have been considered. Each mixture was prepared in a high-pressure variable-volume vessel in which a piston was moved by pressurized nitrogen so as to pressurize the (refrigerant + lubricant) mixture.

First, the apparatus is put into an evacuated vacuum and then weighed using a precision balance (precision: 0.01 g). A calculated amount of TriEGDME is put inside the vessel using a buret. The cell is again connected to a vacuum line for few minutes in order to eliminate the air that could have leaked inside. The vessel is weighed again, and the difference with the initial value gives the mass of TriEGDME added to the system. The apparatus is then connected to a piston pump previously filled with R134a, and a calculated volume of refrigerant is transferred to the vessel. The apparatus is then weighed to ascertain the mass of R134a in the mixture. The mole fraction of the mixture is calculated from the known amounts of the components in the vessel. The uncertainty of the obtained mixture composition is ± 0.0005 in mole fraction.

The mixture is pressurized to a pressure of about 5 MPa and agitated by shaking the vessel, to homogenize it, and it is loaded into the densimeter. This is done in several steps, pumping small amounts of the mixture under pressure from the variable-volume vessel through the densimeter until a constant density is reached.

3. Results

The density was measured for three mixtures with refrigerant mole fractions of 0.9485, 0.9655, and 0.9798. The density was measured at 10 K intervals in the temperature range (283 to 323) K at pressures from (1 to 6) MPa in steps of 1 MPa. To avoid evaporation from the apparatus, at temperatures greater than 303 K the starting pressure was taken about 0.4 MPa greater than the vapor pressure of R134a at the temperature of measurement. The saturation pressure of pure R134a was calculated from the equation of state (EoS) reported by Astina and Sato.[11]

Thirty $p\rho T$ points were obtained for each mixture at fixed composition, giving an overall data set of 90 data points that are listed in Table 1. The densities were correlated using a Tait equation:[12]

$$\rho(T, P) = \frac{\rho_0(T)}{1 - C \ln\left(\frac{B_T + p}{B_T + p_0}\right)} \tag{1}$$

where the dependences on temperature of the reference density ρ_0 and of the parameter B_T are expressed through second-order polynomials:

$$\rho_0(T) = A_0 + A_1 T + A_2 T^2 \tag{2}$$

and

$$B_T = B_0 + B_1 T + B_2 T^2 \tag{3}$$

A value of 1 MPa was chosen for the reference pressure p_0. The coefficients A_i, B_i, and C have been fitted to the experimental data for each composition and the coefficients so obtained are given in Table 2. The experimental density data and the values calculated from the Tait equation defined above are shown in Figure 2 along each isotherm as a function of pressure.

The deviation Δ of each experimental point from the equation is calculated as

$$\Delta_i = \left(\frac{\rho_{\text{exp}} - \rho_{\text{calc}}}{\rho_{\text{exp}}}\right)_i \tag{4}$$

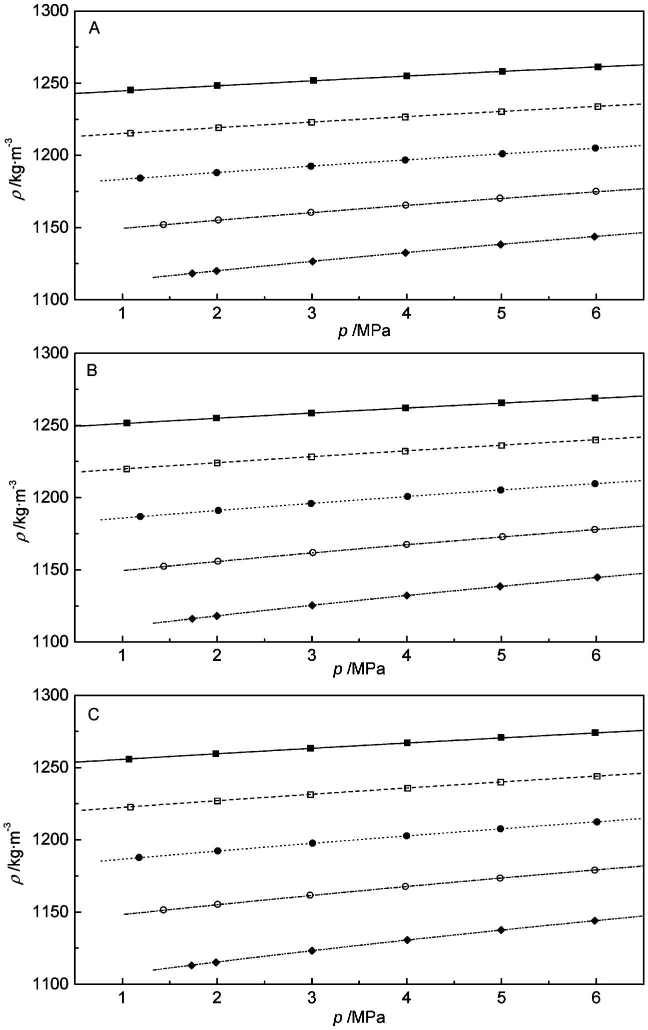

Figure 2. Experimental data of density ρ at three R134a molar compositions x as a function of pressure p for different temperatures T, together with calculated lines from the Tait equation: ■, $T = 283.3$ K; □, $T = 293.3$ K; ●, $T = 303.3$ K; ○, $T = 313.3$ K; ◆, $T = 323.4$ K. A, $x = 0.9485$; B, $x = 0.9655$; C, $x = 0.9798$.

where subscripts exp and calc stand for experimental and calculated values, respectively.

Denoting by NPT the number of experimental points in each set, the following statistical indexes are evaluated: the average absolute deviation (AAD), the bias, the maximum absolute deviation (MAD), and the standard deviation σ

$$\mathrm{AAD}\ (\%) = \frac{100}{\mathrm{NPT}} \sum_{i=1}^{\mathrm{NPT}} |\Delta_i| \tag{5}$$

$$\mathrm{bias}\ (\%) = \frac{100}{\mathrm{NPT}} \sum_{i=1}^{\mathrm{NPT}} \Delta_i \tag{6}$$

$$\mathrm{MAD}\ (\%) = 100\ \max|\Delta_i| \tag{7}$$

and

$$\sigma = \frac{1}{\mathrm{NPT}} \sqrt{\sum_{i=1}^{\mathrm{NPT}} (\Delta_i)^2} \tag{8}$$

Table 3 reports the values of the statistical indexes for the three mixtures, and the deviations are shown in Figure 3. From Table 3 and Figures 2 and 3, one can see that the deviations of the data are low, as evidenced by the AAD values. The experimental points result to fall in a narrow range well-centered with respect to the corresponding equation at each composition. The lines in Figure 2 are smoothed and show a regular trend. Unfortunately, no additional points are available in the same ranges from other researchers, and it was not possible to verify

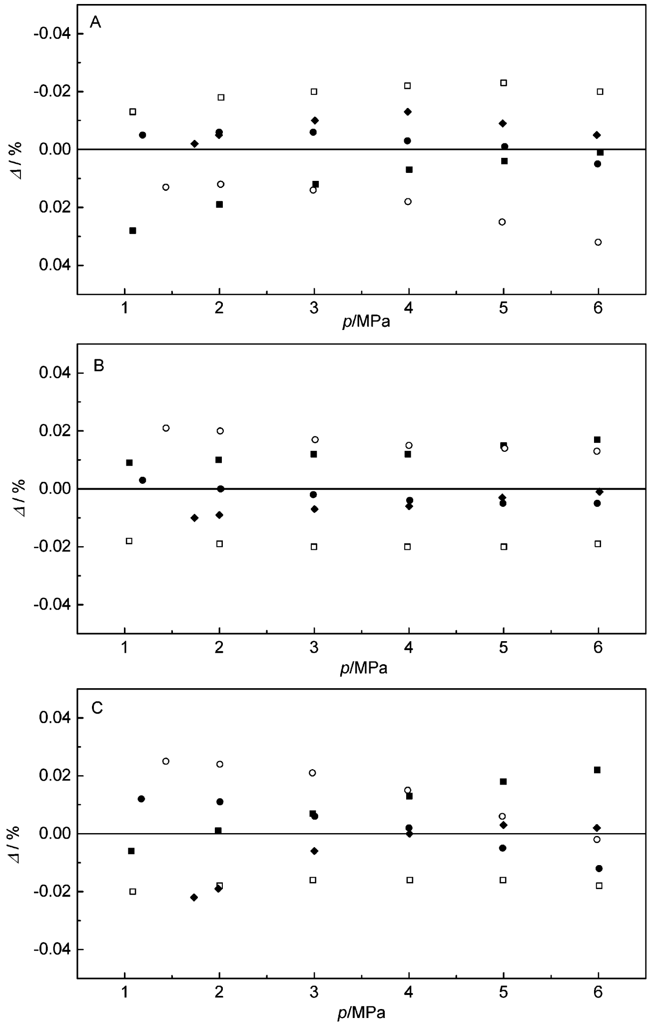

Figure 3. Deviations Δ of the experimental data from the Tait equation for each composition x as a function of pressure p for different temperatures T: ■, $T = 283.3$ K; □, $T = 293.3$ K; ●, $T = 303.3$ K; ○, $T = 313.3$ K; ◆, $T = 323.4$ K. A, $x = 0.9485$; B, $x = 0.9655$; C, $x = 0.9798$.

Table 2. Coefficients of the Tait Equation, Equations 1 to 3, for Three Systems at Constant Molar Composition x

x	0.9485	0.9655	0.9798
p_0/MPa	1.0	1.0	1.0
A_0/kg·m^{-3}	1140.40	1099.06	1125.87
A_1/kg·m^{-3}·K^{-1}	3.56353	4.08490	4.10721
A_2/kg·m^{-3}·K^{-2}	−0.0112805	−0.0125230	−0.0128804
B_0/MPa	182.800	348.735	491.944
B_1/MPa·K^{-1}	−0.748787	−1.80317	−2.70237
B_2/MPa·K^{-2}	0.000663264	0.00233592	0.00375164
C	0.0719337	0.0793999	0.0888895

Table 3. Statistical Analysis of the Deviations between Experimental Data and Values Calculated from the Tait Equation at Each Molar Composition x

x	0.9485	0.9655	0.9798
NPT	30	30	30
AAD (%)	0.012	0.011	0.012
bias (%)	0.000	0.000	0.000
MAD (%)	0.032	0.021	0.025
σ	0.00015	0.00013	0.00014

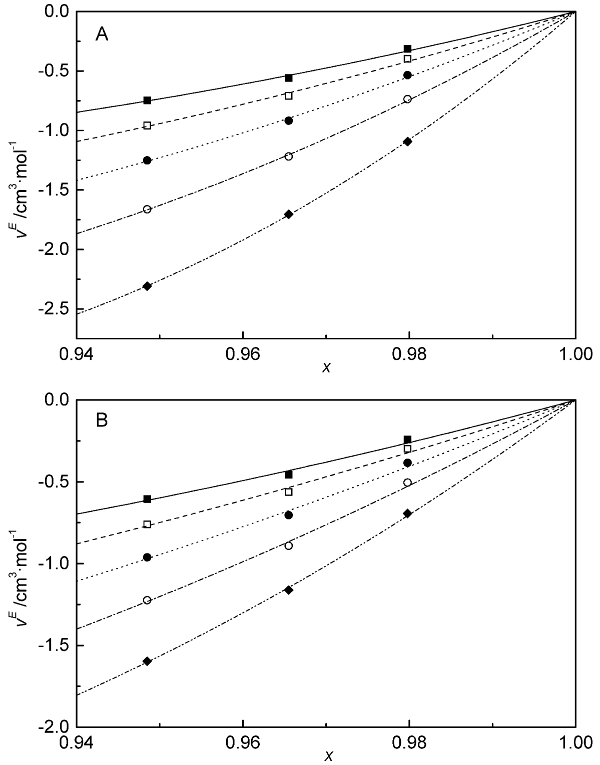

Figure 4. Excess molar volume V^E calculated from the experimental density data at several temperatures T for two conditions of pressure p as a function of R134a molar composition x together with lines from data correlation: ■, $T = 283.3$ K; □, $T = 293.3$ K; ●, $T = 303.3$ K; ○, $T = 313.3$ K; ◆, $T = 323.4$ K. A, $p = 2$ MPa; B, $p = 6$ MPa.

the accuracy of the present measurements through a comparison against values of independent sources.

The calculation of the excess molar volumes V^E from the experimental values has also been performed. The required molar volumes V of the pure components were generated from the Astina and Sato EoS[11] for R134a and from the Tait equation from Comuñas et al.[13] for TriEGDME. The experimental excess molar volumes are represented as a function of molar composition in Figure 4, limiting the analysis to only two isobars. The plotted lines are obtained by fitting the available data at fixed temperature and pressure conditions with a polynomial equation:

$$V^E = C_3x^3 + C_2x^2 - (C_2 + C_3)x \qquad (9)$$

where the two free parameters C_2 and C_3 are regressed to the data. Equation 9 ensures that the excess volume has a null value at $x = 0$ and $x = 1$. Table 4 reports the values of the coefficients C_2 and C_3 for the temperature and pressure conditions at which the experimental points were measured.

The molar volume of the mixture $V_{mix} = M_{mix}/\rho$, where M_{mix} is the mixture molar mass, varies between (81 and 95) cm^3·mol^{-1}, and the effect of nonideality appears to be quite strong since the excess volume amounts to some percent of the overall value even if a quite limited amount of TriEGDME is present in the mixture. This is shown in Figure 5, where the quantity V^E/V_{mix} (i.e., the relative contribution of the excess volume to the overall value of the mixture molar volume) is plotted as a function of molar composition. Moreover, from Figure 4 it is evident that the negative deviations of the mixture molar volume from the ideal behavior become larger with increasing temperature and with decreasing pressure.

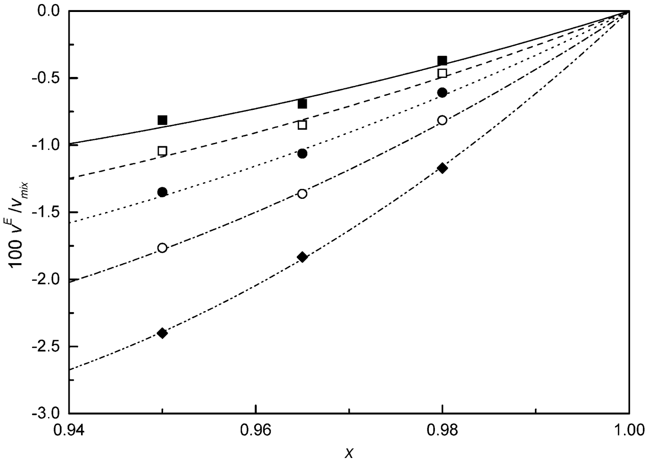

Figure 5. Contribution of the excess volume V^E to the overall molar volume value V_{mix} as a function of R134a molar composition x at pressure $p = 2$ MPa and for several values of temperature T: ■, $T = 283.3$ K; □, $T = 293.3$ K; ●, $T = 303.3$ K; ○, $T = 313.3$ K; ◆, $T = 323.4$ *K*.

Table 4. Coefficients of Equation 9 for Several Values of Temperature *T* and Pressure *p*

T	p	C_2	C_3	T	p	C_2	C_3
K	MPa	cm^3·mol^{-1}	cm^3·mol^{-1}	K	MPa	cm^3·mol^{-1}	cm^3·mol^{-1}
283.3	1.1	−79.854	49.299	303.3	4.0	−63.780	44.291
283.3	2.0	−69.491	43.563	303.3	5.0	−52.662	37.841
283.3	3.0	−58.742	37.638	303.3	6.0	−31.869	26.550
283.3	4.0	−46.771	31.125	313.3	1.4	−223.926	133.341
283.3	5.0	−39.722	27.159	313.3	2.0	−198.601	119.436
283.3	6.0	−32.906	23.335	313.3	3.0	−152.623	94.487
293.3	1.1	−86.7581	55.286	313.3	4.0	−118.023	75.528
293.3	2.0	−70.230	46.191	313.3	5.0	−82.903	56.456
293.3	3.0	−55.060	37.831	313.3	6.0	−64.838	46.220
293.3	4.0	−39.855	29.494	323.4	1.7	-461.517	261.760
293.3	5.0	−30.355	24.110	323.4	2.0	−429.212	244.503
293.3	6.0	−20.832	18.773	323.4	3.0	−335.233	193.930
303.3	1.2	−135.566	83.596	323.4	4.0	−257.509	152.107
303.3	2.0	−109.852	69.596	323.4	5.0	−200.885	121.391
303.3	3.0	−86.666	56.819	323.4	6.0	−150.860	94.261

4. Conclusions

The density in the liquid phase of three binary mixtures of R134a and TriEGDME has been measured with a vibrating-tube densimeter at temperatures in the range (283 to 323) K at pressures between (1 and 6) MPa with mole fractions of R134a of 0.9485, 0.9655, and 0.9798. These compositions cover the operating conditions of a compression refrigeration plant that would use a refrigerant fluid mixed with a lubricant. The data have been correlated using a Tait equation for each composition resulting in very low deviations and regular trends. The analysis of the excess volumes has evidenced the strong deviation of that system from the ideal behavior.

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Literature Cited

(1) Coronas, A.; Mainar, A. M.; Patil, K. R.; Conesa, A.; Shen, S.; Zhu, S. Solubility of 1,1,1,2-tetrafluoroethane in triethylene glycol dimethyl ether. *J. Chem. Eng. Data* **2002**, *47*, 56−58.

(2) Park, Y. M.; Kang, J. O.; Yoo, J.; Lee, J. W. Vapor pressure of the 1,1,1,2-tetrafluoroethane (R134a) + polyalkylene glycol system. *Int. J. Thermophys.* **2004**, *25*, 1849−1861.

(3) López, E. R.; Mainar, A. N.; García, J.; Urieta, J. S.; Fernandéz, J. Experimental and predicted solubilities of HFC134a (1,1,1,2-tetrafluoroethane) in polyethers. *Ind. Eng. Chem. Res.* **2004**, *43*, 1523−1529.

(4) Marchi, P.; Scalabrin, G.; Horstmann, S.; Ihmels, E. C.; Fischer, K.; Gmehling, J. Bubble pressure measurements for (1,1,1,2-tetrafluoroethane + triethylene glycol dimethyl ether) system. *J. Chem. Thermodyn*. **2006**, in press.
(5) Comuñas, M. J. P.; Fernández, J. A.; Baylaucq, A.; Canet, X.; Boned, C. *PρTx* measurements for HFC-134a + triethylene glycol dimethyl ether system. *Fluid Phase Equilib.* **2002**, *199*, 185−195.
(6) Monsalvo, M. A.; Baylaucq, A.; Reghem, P.; Quiñones-Cisneros, S. E.; Boned, C. Viscosity measurements and correlations of binary mixtures: 1,1,1,2-tetrafluoroethane (HFC-134a) + tetraethylene glycol dimethyl ether (TEGDME). *Fluid Phase Equilib.* **2005**, *233*, 1−8.
(7) Ihmels, E. C.; Gmehling, J. Densities of toluene, carbon dioxide, carbonyl sulfide, and hydrogen sulfide over a wide temperature and pressure range in the sub- and supercritical state. *Ind. Eng. Chem. Res.* **2001**, *40*, 4470−4477.
(8) Ihmels, E. C.; Gmehling, J. Densities of sulfur hexafluoride and dinitrogen monoxide over a wide temperature and pressure range in the sub- and supercritical states. *Int. J. Thermophys.* **2002**, *23*, 709−743.
(9) Ihmels, E. C. Experimentelle bestimmung, korrelation und vorhersage von dichten und dampfdrücken. Ph.D. Dissertation, University of Oldenburg, Aachen, 2002.
(10) Ihmels, E. C.; Fischer, K.; Gmehling, J. Thermodynamic properties of the butenes. Part I. Experimental densities, vapor pressures, and critical points. *Fluid Phase Equilib.* **2005**, *228*−*229*, 155−171.
(11) Astina, I. M.; Sato, H. A fundamental equation of state for 1,1,1,2-tetrafluoroethane with an intermolecular potential energy background and reliable ideal-gas properties. *Fluid Phase Equilib.* **2004**, *221*, 103−111.
(12) Dymond, J. H.; Malhotra, R. The Tait equation: 100 years on. *Int. J. Thermophys*. **1988**, *9*, 941−951.
(13) Comuñas, M. J. P.; López, E. R.; Pires, P.; García, J.; Fernández, J. *PρT* measurements of polyethylene glycol dimethylethers between 278.15 and 328.15 K at pressures to 12 MPa. *Int. J. Thermophys.* **2000**, *21*, 831−851.

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