J. Chem. Eng. Data **2004,** *49,* 1344−1349

High-Pressure Volumetric Properties of Three Monoethylene Glycol Alkyl Ethers

María J. P. Comuñas,*,† Patrick Reghem,‡ Antoine Baylaucq,‡ Christian Boned,‡ and Josefa Fernández†

Laboratorio de Propiedades Termofísicas, Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago de Compostela, E-15782 Santiago de Compostela, Spain, and Laboratoire des Fluides Complexes, UMR CNRS 5150, Faculté des Sciences, BP 1155, F-64013 Pau Cedex, France

In the present work, the effect of pressure and temperature on the density, isobaric thermal expansivity, α_p, isothermal compressibility, κ_T, and internal pressure, π of monoethylene glycol methyl ether (MEGME), monoethylene glycol ethyl ether (MEGEE), and monoethylene glycol isopropyl ether (iso-MEGPE) has been determined. New density data (273 experimental points) have been obtained with a vibrating tube densimeter at temperatures between (293.15 and 353.15) K and pressures up to 60 MPa. The trend of the volumetric properties with the number of methylene groups in the monoethylene glycol alkyl ether molecules has been analyzed. The ability of different equations of state to predict the volumetric properties of these molecules has been tested.

Introduction

A knowledge of thermophysical properties is very important in many practical problems concerning heat transport and fluid flow. Our research concerning polyalkylene glycol polyalkyl ethers aims to create a complete database of thermodynamic and transport properties for these fluids, which could be used to develop models able to represent accurately the behavior with both temperature and pressure of the thermophysical properties of these interesting compounds. As a part of our studies on polyalkylene glycol polyalkyl ethers, the density and dynamic viscosity of several poly(ethylene glycol) dimethyl ethers[1−6] (monoethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether) are reported up to (60 and 100) MPa, respectively. Moreover, densities for several diethylene glycol monoalkyl ethers[7] (diethylene glycol monomethyl ether and diethylene glycol monoethyl ether) up to 25 MPa and the speed of sound of triethylene glycol dimethyl ether and tetraethylene glycol dimethyl ether up to 100 MPa[8] have recently been published.

The present work was undertaken with the aim to complete our database. The volumetric behavior of monoethylene glycol methyl ether (MEGME), monoethylene glycol ethyl ether (MEGEE), and monoethylene glycol isopropyl ether (iso-MEGPE) is analyzed. The influence of the chain length (number of methylene groups) is considered. These products have been actively studied for various applications. For example, the phase equilibrium behavior of high-molecular-weight alcohols, such as monoethylene glycol ethyl ether, with CO_2 is essential to process development in the food and cosmetic industries.[9,10]

Density measurements for monoethylene glycol alkyl ethers at atmospheric pressure have previously been reported by several authors, but a survey of the literature shows a lack of thermodynamic data for pressures higher than atmospheric. Concerning the studies at atmospheric pressure, Cocchi et al.[11] have reported density values for MEGME from (263.15 to 353.15) K; Ferrari et al.,[12] from (288.15 to 318.15) K; Kinart et al.,[13] between (291.15 and 308.15) K; Pal and Sharma,[14] at (298.15 and 308.15) K; and George and Sastry,[15] between (298.15 and 313.15) K. The density values for MEGEE have been published by, among other authors, George and Sastry[15] from (298.15 to 313.15) K and Tamura et al.[16] at (298.15 and 303.15) K. Finally, for iso-MEGPE Pal and Bhardwaj[17,18] and Tamura et al.[16] reported the density from (298.15 to 318.15) K and at (298.15 and 303.15) K, respectively.

In this paper, density data for MEGME, MEGEE, and iso-MEGPE are reported at temperatures between (293.15 and 353.15) K and at pressures up to 60 MPa. From the density data, the isobaric thermal expansivity, α_p, the isothermal compressibility, κ_T, and the internal pressure, π, have been determined, and an analysis of the trends in these properties with respect to the temperature, the pressure, and the number of methylene groups in the monoethylene glycol alkyl ether molecules has been performed.

Experimental Section

Materials. Monoethylene glycol methyl ether, MEGME, (CAS number 109-86-4, principal name 2-methoxyethanol, and $M_w = 76.10$ g·mol^{-1}) and monoethylene glycol isopropyl ether, iso-MEGPE, (CAS number 109-59-1, principal name 2-iso-propoxyethanol, and $M_w = 104.15$ g·mol^{-1}) were obtained from Aldrich with purities of 99.3% and 99%, respectively. Monoethylene glycol ethyl ether, MEGEE, (CAS number 110-80-5, principal name 2-ethoxyethanol, $M_w = 90.10$ g·mol^{-1}) was obtained from Riedel de Haën with a purity of 99%. These chemicals were subjected to no further purification.

---

* To whom correspondence should be addressed. E-mail: famajose@usc.es.

† Universidad de Santiago de Compostela.

‡ UMR CNRS 5150.

10.1021/je049929f CCC: $27.50

Measurement Technique. Densities as a function of pressure and temperature were determined using an Anton Paar DMA 60/512P vibrating tube densimeter. All of the devices used for both the filling of the densimeter cell and the measurements have been presented previously.[5] The temperature of the vibrating tube is controlled with a thermoregulated liquid bath (Julabo Paratherm). The temperature is measured inside the cell block with an AOIP 5207 thermometer that was calibrated to within ±0.05 K (ITS-90). The pressure was measured with a Hottinger Baldwin Messtechnik (HBM) manometer with an uncertainty of ±0.05 MPa. The calibration parameters of the densimeter cell were determined using the better of the two calibration methods proposed by Lagourette et al.[19] This procedure is based on water as a reference substance and also requires a knowledge of the periods of the cell under vacuum as a function of temperature. For water, the density values reported by Kell and Whalley[20] with an uncertainty of 10^{-5} g·cm^{-3} have been used. Taking into account the temperature, pressure, and water density accuracies, we report the total uncertainty in our experimental density to be 1×10^{-4} g·cm^{-3}.

Concerning the reference density values of water reported by Kell and Whalley, it is necessary to point out that the temperature scale used by these authors was the IPTS-68. A comparison of the IPTS-68 with the temperature scale that we used (ITS-90) has been performed over the temperature range of our measurements, taking into account the coefficients recalculated by Preston-Thomas[21] and by McGlashan.[22] The differences between both temperature scales, over the experimental temperature range analyzed in the present work, range from 0.005 K at 293.15 K up to 0.019 K at 353.15 K. These differences are lower than the used thermometer accuracy. Then, the density reference values of water from the data reported by Kell and Whalley were recalculated, introducing the correction in temperature from IPTS 68 to ITS 90. The result was that the differences between both scales cause a difference in water density of 6×10^{-6} g·cm^{-3}. The calibration of the densimeter has been done using the new reference density values for water, and an uncertainty of 6×10^{-6} g·cm^{-3} has been found in the experimental density of MEGME, DEGEE, and iso-MEGPE. Therefore, the uncertainty due to the correction in the temperature scale is markedly lower than the estimated experimental uncertainty of the measurements, $\pm 1 \times 10^{-4}$ g·cm^{-3}.

In addition, the differences between the density water reference values proposed by Span[23] and those of Kell and Whalley[20] show an average deviation between both data sets of 4×10^{-6} g·cm^{-3} over the entire temperature and pressure intervals analyzed in this work. If the water density values obtained from the equation of state of Span are used to perform the densimeter calibration, then the experimental densities of MEGME, DEGEE, and iso-MEGPE agree with the values obtained by using the Kell and Whalley data within an average deviation of 4×10^{-6} g·cm^{-3}. In conclusion, the uncertainty that introduces the use of the values due to Span[23] instead of the values reported by Kell and Whalley is markedly lower than our densimeter technique uncertainty.

Results and Discussion

The measured densities of MEGME, DEGEE, and iso-MEGPE are reported in Table 1 along isotherms between (293.15 and 353.15) K at pressures up to 60 MPa. To correlate our values over the entire temperature and pressure interval, as in previous work,[1,2] the following Tait-like equation has been used:

$$\rho(T, p) = \frac{A_0 + A_1 T + A_2 T^2 + A_3 T^3}{1 - C \ln\left(\dfrac{B_0 + B_1 T + B_2 T^2 + p}{B_0 + B_1 T + B_2 T^2 + 0.1\ \mathrm{MPa}}\right)} \tag{1}$$

where the A_i parameters for each monoethylene glycol alkyl ether are obtained by correlating the density values at atmospheric pressure against the temperature and then the C and B_i coefficients are calculated by adjusting, for each compound, the density values against both the temperature and the pressure (which are different from the atmospheric values).

To compare the experimental density values with those obtained with the Tait-correlation, either reported by other authors or predicted with several equations of state, we have used, as in previous work,[5] the absolute average percentage deviation (AAD), the maximum percentage deviation (DMAX), and the average percentage deviation (Bias), which are defined as

$$\mathrm{AAD} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{theo}}}{\rho_i^{\mathrm{exp}}}\right| \tag{2}$$

$$\mathrm{DMAX} = \max\left(100\left|\frac{\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{theo}}}{\rho_i^{\mathrm{exp}}}\right|\right) \tag{3}$$

$$\mathrm{bias} = \frac{100}{N}\sum_{i=1}^{N}\frac{\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{theo}}}{\rho_i^{\mathrm{exp}}} \tag{4}$$

The parameters of eq 1, obtained for the Tait correlation of the three monoethylene glycol alkyl ethers and the standard deviation, σ, AAD, DMAX, and bias are shown in Table 2. Notice that the standard deviation is of the same order as the experimental uncertainty. Equation 1 permits interpolation to determine the density at other temperatures and pressures. As already indicated, no study about density at high pressures has been found in the literature for these substances. However, some comparison with the literature data at atmospheric pressure can be made.

Our experimental values for MEGME at atmospheric pressures present an average deviation of 0.06% with the data reported by Cocchi et al.[11] and 0.04% with both the data of Ferrari et al.[12] and of Kinart et al.[13] The comparison with the data of Pal and Sharma[14] gives an AAD of 0.06%, whereas the comparison with the data of George and Sastry[15] gives relative deviations of −0.03%, −0.03%, −0.31%, and −0.05% at (298.15, 303.15, 308.15, and 313.15) K, respectively. The largest deviation (−0.31%) is found at 308.15 K with the last authors, but in this sense it must be pointed out that the density data of Cocchi et al.[11] and Pal and Sharma[14] at 308.15 K also present high relative deviations (−0.26% and −0.22%) with the experimental values of George and Sastry.

For MEGEE, the experimental values at atmospheric pressure reported in this work present relative deviations of 0.02% and −0.01% with the data reported by Tamura et al.[16] at (298.15 and 303.15) K, respectively. Moreover, the relative deviations with the density values of George and Sastry[15] are −0.01%, −0.06%, −0.26%, and −0.04%

Table 1. Experimental Densities as a Function of Temperature, *T*, and Pressure, *p*

	T K						
p MPa	293.15	303.15	313.15	323.15	333.15	343.15	353.15
	ρ g·cm^{-3}						
	Monoethylene Glycol Methyl Ether						
0.1	0.9645	0.9554	0.9459	0.9363	0.9267	0.9171	0.9071
5	0.9675	0.9584	0.9493	0.9402	0.9309	0.9212	0.9117
10	0.9707	0.9618	0.9527	0.9439	0.9346	0.9253	0.9161
15	0.9738	0.9651	0.9563	0.9474	0.9384	0.9293	0.9201
20	0.9766	0.9680	0.9595	0.9508	0.9419	0.9329	0.9240
25	0.9795	0.9711	0.9625	0.9540	0.9453	0.9369	0.9279
30	0.9823	0.9740	0.9656	0.9572	0.9488	0.9402	0.9315
35	0.9851	0.9769	0.9685	0.9605	0.9520	0.9436	0.9349
40	0.9877	0.9796	0.9715	0.9633	0.9550	0.9468	0.9387
45	0.9903	0.9823	0.9744	0.9663	0.9580	0.9500	0.9418
50	0.9929	0.9848	0.9770	0.9691	0.9610	0.9531	0.9451
55	0.9953	0.9875	0.9795	0.9719	0.9639	0.9562	0.9482
60	0.9977	0.9899	0.9822	0.9746	0.9668	0.9590	0.9512
	Monoethylene Glycol Ethyl Ether						
0.1	0.9296	0.9207	0.9113	0.9018	0.8923	0.8826	0.8726
5	0.9329	0.9240	0.9149	0.9058	0.8965	0.8872	0.8776
10	0.9362	0.9274	0.9185	0.9097	0.9005	0.8914	0.8820
15	0.9393	0.9307	0.9221	0.9134	0.9045	0.8956	0.8865
20	0.9424	0.9339	0.9255	0.9169	0.9082	0.8994	0.8906
25	0.9452	0.9370	0.9287	0.9203	0.9118	0.9034	0.8948
30	0.9482	0.9399	0.9318	0.9236	0.9154	0.9069	0.8985
35	0.9511	0.9429	0.9349	0.9269	0.9187	0.9105	0.9020
40	0.9537	0.9458	0.9378	0.9300	0.9218	0.9138	0.9059
45	0.9565	0.9486	0.9407	0.9330	0.9250	0.9172	0.9088
50	0.9590	0.9513	0.9434	0.9357	0.9279	0.9204	0.9125
55	0.9616	0.9538	0.9461	0.9387	0.9311	0.9234	0.9157
60	0.9640	0.9563	0.9489	0.9414	0.9339	0.9265	0.9187
	Monoethylene Glycol Isopropyl Ether						
0.1	0.9040	0.8950	0.8855	0.8759	0.8664	0.8568	0.8468
5	0.9073	0.8984	0.8892	0.8801	0.8710	0.8615	0.8519
10	0.9108	0.9021	0.8932	0.8843	0.8752	0.8661	0.8567
15	0.9141	0.9055	0.8969	0.8882	0.8794	0.8705	0.8616
20	0.9173	0.9088	0.9004	0.8919	0.8833	0.8747	0.8658
25	0.9204	0.9121	0.9037	0.8954	0.8870	0.8786	0.8700
30	0.9236	0.9152	0.9072	0.8990	0.8907	0.8825	0.8741
35	0.9264	0.9182	0.9102	0.9023	0.8942	0.8861	0.8778
40	0.9292	0.9212	0.9133	0.9054	0.8974	0.8895	0.8816
45	0.9320	0.9240	0.9162	0.9085	0.9007	0.8931	0.8852
50	0.9345	0.9270	0.9191	0.9114	0.9036	0.8964	0.8883
55	0.9371	0.9297	0.9219	0.9145	0.9069	0.8994	0.8917
60	0.9396	0.9321	0.9248	0.9173	0.9100	0.9025	0.8949

Table 2. Parameters and Deviations for Density Correlation by Using Equation 1

coefficients	MEGME	MEGEE	iso-MEGPE
A_0/g·cm^{-3}	1.1447	1.0829	1.0709
A_1/g·cm^{-3}·K^{-1}	-2.0371×10^{-4}	-3.1530×10^{-5}	-1.0915×10^{-4}
A_2/g·cm^{-3}·K^{-2}	-1.7568×10^{-6}	-2.0634×10^{-6}	-1.9698×10^{-6}
A_3/g·cm^{-3}·K^{-3}	1.2145×10^{-9}	1.3221×10^{-9}	1.3650×10^{-9}
C	0.085549	0.084198	0.083257
B_0/MPa	559.4085	458.9998	470.1058
B_1/MPa·K^{-1}	−2.0968	−1.5862	−1.7540
B_2/MPa·K^{-2}	2.1192×10^{-3}	1.3995×10^{-3}	1.7251×10^{-3}
deviations			
σ/g·cm^{-3}	1×10^{-4}	1×10^{-4}	1×10^{-4}
AAD/%	1×10^{-2}	1×10^{-2}	1×10^{-2}
DMAX/%	2×10^{-2}	4×10^{-2}	3×10^{-2}
bias/%	2×10^{-4}	7×10^{-5}	5×10^{-4}

at (298.15, 303.15, 308.15, and 313.15) K, respectively. The largest deviation is also found with the data of George and Sastry at 308.15 K.

Finally, for iso-MEGPE the average deviations with the data of Tamura et al.[16] and Pal and Bhardwaj[17,18] are 0.03% and 0.19%, respectively.

The isobaric thermal expansivity, $\alpha_p = -(1/\rho)(\partial\rho/\partial T)_p$, the isothermal compressibility, $\kappa_T = (1/\rho)(\partial\rho/\partial p)_T$, and the internal pressure, $\pi = T(\alpha_p/\kappa_T) - p$, for the three monoethylene glycol alkyl ethers were determined from the Tait-like correlations $\rho(T, p)$ using the parameters of Table 2. The estimated uncertainties are $\pm 0.2 \times 10^{-4}$ K^{-1} for the isobaric thermal expansivity, between $\pm 0.05 \times 10^{-4}$ MPa^{-1} and $\pm 0.10 \times 10^{-4}$ MPa^{-1} for the isothermal compressibility, and 1% for the internal pressure. Table 3 summarizes the calculated values for the isobaric thermal expansivity and the isothermal compressibility. As shown in Figure 1, at fixed pressure the isobaric thermal expansivity and the isothermal compressibility increase with increasing temperature and at a fixed temperature decrease with increasing pressure. Both thermophysical properties have their lowest values for MEGME and their highest values for iso-MEGPE (i.e., these properties increase when the number of methylene groups increases). Similar behavior has been found for several diethylene glycol monoalkyl ethers.[7]

As shown in Figures 2 and 3, contrary to the isobaric thermal expansivity and the isothermal compressibility, the internal pressure has its lowest values for iso-MEGPE and the highest ones for MEGME. Similar behavior has been found for diethylene glycol monoalkyl ethers for which López et al.[7] have found higher values for diethylene glycol monomethyl ether than for diethylene glycol monoethyl ether. When the number of methylene groups (nonpolar) increases, the internal pressure decreases. On the contrary, it has been observed[5] for several poly(ethylene glycol) dimethyl ethers that the internal pressure increases when the number of ethylene glycol groups increases, that is, the number of polar group increases. In Figure 3, the values reported previously by Comuñas et al.[5] for monoethylene glycol dimethyl ether (MEGDME) have also been plotted, being that their π values are lower than those of MEGME. This is due to the fact that the monoethylene glycol alkyl ether molecules exhibit a strong ability to form hydrogen bonds because the molecule have hydrogen bond donors on the hydrogen atom of the OH group and acceptors on the oxygen atoms, whereas the polyethers as MEGDME do not have any OH groups.

The capability of Soave−Redlich−Kwong with the volume translation of Peneloux (SRK−VT),[24,25] translation-modified Peng−Robinson (t-mPR),[26] and Patel−Teja (PT)[27] equations of state (EOS) for density predictions of these compounds has been tested. The values of the critical pressure, p_c, critical temperature, T_c, and acentric factor, ω, have been taken from the literature or estimated. For MEGME, the critical point, experimentally determined (visual in glass tube) by Wilson et al.[28] ($p_c = 5.285$ MPa and $T_c = 597.6$ K) has been considered. Concerning the acentric factor, it has been obtained from the experimental vapor pressure values published by Pick et al.[29] ($\omega = 0.454$). For MEGEE and iso-MEGPE, no experimental values of their critical properties have been found in the literature. The experimental saturation curves have been reported in the literature by Riddick et al.[30] for MEGEE and by Dykyj et al.[31] for iso-MEGPE. To estimate the critical properties of MEGEE and iso-MEGPE among different contribution methods for the estimation of critical properties, the Lydersen[32] method is chosen for p_c and the Klincewicz[33] method is chosen for T_c. The reason for this choice is that for MEGME the critical properties obtained with these methods are closer to the experimental ones[28] than other estimation methods for critical properties. The obtained values are 4.18 MPa and 611.27 K for MEGEE and 3.62 MPa and 604.52 K for iso-MEGPE. Concerning the acentric

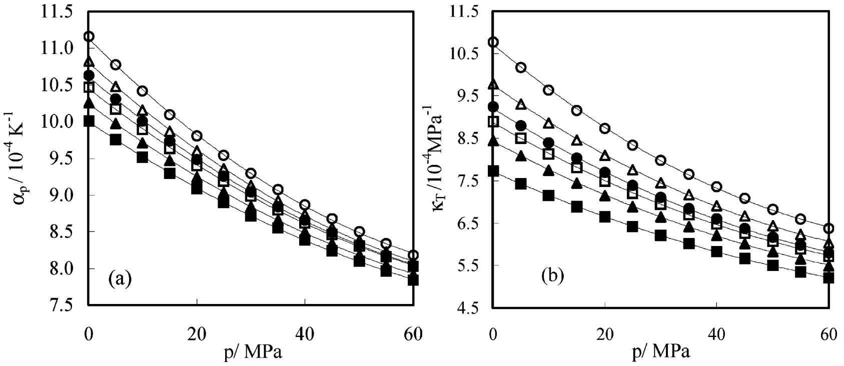

Figure 1. Variation of the (a) isobaric thermal expansion coefficient, α_P, and of the (b) isothermal compressibility, κ_T, with pressure: □, MEGME; △, MEGEE; and ○, iso-MEGPE. Solid and open symbols are the values at (313.15 and 333.15) K, respectively.

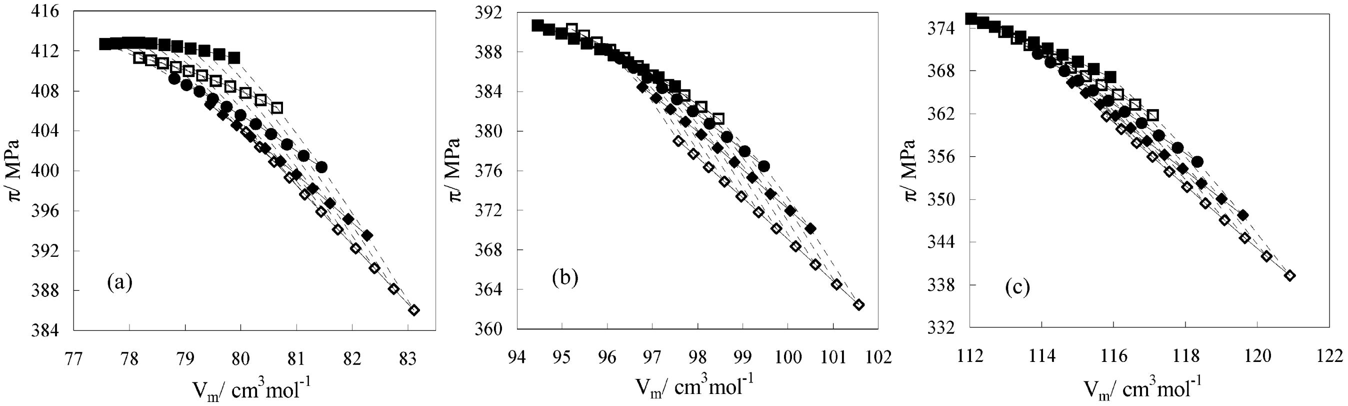

Figure 2. Variation of the internal pressure, π, with molar volume at different temperatures and pressures for (a) MEGME, (b) MEGEE, (c) and iso-MEGPE: ■, 303.15 K; □, 313.15 K; ●, 323.15 K; ◆, 333.15 K; ◇, 343.15 K; and - - - - - -, isobars from 5 to 55 MPa at 5 MPa intervals.

Table 3. Isobaric Thermal Expansivity, α_p, and Isothermal Compressibility, κ_T, at Different Temperatures, *T*, and Pressures, *p*

	T K									
	303.15		313.15		323.15		333.15		343.15	
p MPa	$10^4\,\alpha_p$ K^{-1}	$10^4\,\kappa_T$ MPa^{-1}	$10^4\,\alpha_p$ K^{-1}	$10^4\,\kappa_T$ MPa^{-1}	$10^4\,\alpha_p$ K^{-1}	$10^4\,\kappa_T$ MPa^{-1}	$10^4\,\alpha_p$ K^{-1}	$10^4\,\kappa_T$ MPa^{-1}	$10^4\,\alpha_p$ K^{-1}	$10^4\,\kappa_T$ MPa^{-1}
	Monoethylene Glycol Methyl Ether									
10	9.32	6.70	9.52	7.15	9.71	7.62	9.89	8.13	10.07	8.68
20	8.92	6.26	9.09	6.64	9.25	7.05	9.40	7.49	9.56	7.95
30	8.58	5.87	8.72	6.21	8.85	6.57	8.99	6.95	9.12	7.34
40	8.27	5.53	8.39	5.83	8.51	6.15	8.62	6.48	8.74	6.83
50	7.99	5.23	8.10	5.50	8.21	5.78	8.31	6.07	8.41	6.38
	Monoethylene Glycol Ethyl Ether									
10	9.48	7.27	9.71	7.75	9.94	8.28	10.16	8.86	10.37	9.50
20	9.05	6.74	9.24	7.15	9.43	7.60	9.60	8.09	9.76	8.63
30	8.67	6.29	8.84	6.65	9.00	7.04	9.13	7.45	9.25	7.90
40	8.35	5.89	8.49	6.21	8.62	6.55	8.73	6.91	8.82	7.30
50	8.06	5.55	8.19	5.83	8.29	6.13	8.38	6.44	8.45	6.78
	Monoethylene Glycol Isopropyl Ether									
10	9.79	7.85	10.01	8.40	10.22	8.99	10.42	9.64	10.61	10.34
20	9.31	7.23	9.49	7.69	9.65	8.19	9.81	8.73	9.95	9.30
30	8.90	6.71	9.04	7.11	9.18	7.53	9.30	7.98	9.41	8.46
40	8.54	6.26	8.66	6.60	8.77	6.97	8.87	7.36	8.96	7.76
50	8.22	5.87	8.33	6.17	8.42	6.49	8.50	6.83	8.57	7.18

factor, it has been obtained from the experimental vapor pressure curves[30,31] and gives $\omega = 0.361$ for MEGEE and $\omega = 0.454$ for iso-MEGPE.

The deviations obtained for the $p\rho T$ EOS prediction are presented in Table 4. The best results are obtained with the PT EOS for which the AADs are 0.6, 7.0, and 0.6% and the DMAX are 1.4, 8.2, and 1.9% for MEGME, MEGEE, and iso-MEGPE, respectively. For PT and t-mPR EOS, the largest deviations are obtained for MEGEE. Notice that the critical pressure and temperature of this compound have been estimated because experimental data are not available. The predicted densities over all of the analyzed pT conditions are lower (AAD = bias > 0) than the experimental ones for MEGME, MEGEE, and iso-MEGPE with t-mPR and for MEGEE in the case of PT and SRK−VT EOS. For MEGME and MEGPE in the case of PT EOS, the calculated values are either above or below the experimental values and AAD is different from bias.

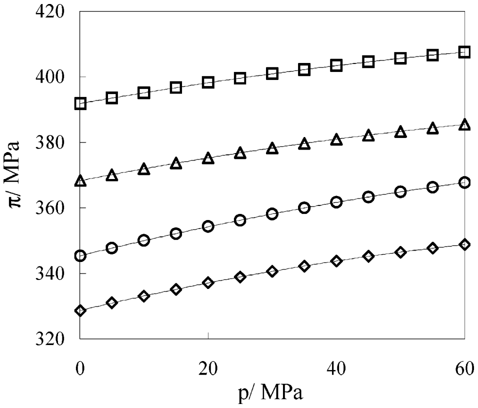

Figure 3. Variation with pressure of the internal pressure, π, for the three monoethylene glycol alkyl ethers at 333.15 K: □, MEGME; △, MEGEE; ○, iso-MEGPE; and ◇[5], the polyether MEGDME.

Table 4. Results for the $p\rho T$ Prediction with Several Equations of State

	AAD %	bias %	DMAX %
liquid		SRK-VT	
MEGME	4.7	−4.7	5.2
MEGEE	4.2	4.2	5.0
iso-MEGPE	4.1	−4.1	5.2
		t-mPR	
MEGME	3.7	3.7	4.8
MEGEE	8.4	8.4	9.5
iso-MEGPE	4.2	4.2	5.6
		PT	
MEGME	0.6	−0.3	1.4
MEGEE	7.0	7.0	8.2
iso-MEGPE	0.6	0.4	1.9

Conclusions

The pressure and temperature trends in the volumetric properties of MEGME, MEGEE, and iso-MEGPE have been analyzed in the temperature range from (293.15 to 353.15) K and the pressure range from (0.1 to 60) MPa on the basis of density measurements. The isobaric thermal expansivities and the isothermal compressibilities increase when the number of methylene groups in the hydroxyether molecule rises. For the internal pressure, the sequence with the chain is the opposite. This means that when the length of hydroxyether rises the liquids become more expansible and more compressible whereas the volume dependence of the internal energy becomes lower. The prediction of the density with SRK−VT, t-mPR, and PT equations of state have been checked, obtaining for MEGME and iso-MEGPE the best results with PT EOS and for MEGEE with SRK−VT EOS.

Acknowledgment

This work was supported by the Spanish Science and Technology Ministry (PPQ2001-3022 and PPQ 2002-3262), European Union (FEDER), Xunta de Galicia (PGIDIT03-PXIC20608PN and PGIDIT03PXIC20609PN), and Spanish−French Joint Action (HF 2001-0101 and 04238PG).

Literature Cited

(1) 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.

(2) Comuñas, M. J. P.; Baylaucq, A.; Boned, C.; Fernández, J. High-Pressure Measurements of the Viscosity and Density of Two Polyethers and Two Dialkyl Carbonates. *Int. J. Thermophys.* **2001**, *22*, 749−768.

(3) Comuñas, M. J. P.; Baylaucq A.; Boned, C.; Canet, X.; Fernández, J. High-Pressure Volumetric Behavior of x 1,1,1,2-Tetrafluoroethane + (1 − x) 2,5,8,11,14-Pentaoxapentadecane (TEGDME) Mixtures. *J. Chem. Eng. Data* **2002**, *47*, 233−238.

(4) Comuñas, M. J. P.; Fernández, J.; Baylaucq, A.; Canet, X.; Boned, C. PρTx Measurements for HFC-134a + Triethylene Glycol Dimethylether System. *Fluid Phase Equilib.* **2002**, *199*, 185−195.

(5) Comuñas, M. J. P.; Baylaucq, A.; Boned, C.; Fernández, J. Volumetric Properties of Monoethylene Glycol Dimethyl Ether and Diethylene Glycol Dimethyl Ether up to 60 MPa. *J. Chem. Eng. Data* **2003**, *48*, 1044−1049.

(6) Baylaucq, A.; Comuñas, M. J. P.; Fernández, J.; Boned, C.; Allal, A. High-Pressure Viscosity and Density Modeling of two Polyethers and two Dialkyl Carbonates. *Fluid Phase Equilib.* **2002**, *199*, 249−263.

(7) López, E. R.; Lugo, L.; Comuñas, M. J. P.; García, J.; Fernández, J. Liquid Density Measurements of Diethylene Glycol Monoalkyl Ethers as a Function of Temperature and Pressure. *J. Chem. Eng. Data* **2004**, *49*, 376−379.

(8) López, E. R.; Daridon, J. L.; Baylaucq, A.; Fernández, J. Thermophysical Properties of Two Poly(alkylene glycol) Derivative Lubricants from High-Pressure Acoustic Measurements. *J. Chem. Eng. Data* **2003**, *48*, 1208−1213.

(9) Stanby, A.; Mollerup, J. Mutual solubilities of mono-alcohols and carbon dioxide: A review of experimental data. *Fluid Phase Equilib.* **1993**, *89*, 351−381.

(10) Joung, S. N.; Yoo, C. W.; Shin, H. Y.; Kim, S. Y.; Yoo, K. P.; Lee, C. S.; Huh, W. S. Measurements and Correlation of High-Pressure VLE of Binary CO_2-Alcohol Systems (methanol, ethanol, 2-methoxethanol and 2-ethoxyethanol). *Fluid Phase Equilib.* **2001**, *185*, 219−230.

(11) Cocchi, M.; Manfredini, M.; Marchetti, A.; Sighinolfi, S.; Tassi, L. The ethane-1,2-diol + 2- methoxyethanol + 1,2-dimethoxyethane ternary solvents system: density and volume properties at different temperatures. *Phys. Chem. Liq.* **2001**, *39*, 481−498.

(12) Ferrari, G.; Foca, G.; Manfredini, M.; Manzini, D.; Marchetti, A.; Tassi, L.; Uldici, A. Density and Volume Properties of the 2-Chloroethanol + 2-Methoxyethanol + 1,2-Dimethoxyethane Ternary Solvent System at Different Temperatures. *J. Solution Chem.* **2003**, *32*, 93−116.

(13) Kinart, C. M.; Kinart, W. J.; Cwiklinska, A. 2-Methoxyethanol-tetrahydrofuran-binary liquid system: viscosities, densities, excess molar volumes and excess Gibbs activation energies of viscous flow at various temperatures. *J. Therm. Anal. Calorim.* **2002**, *68*, 307−317.

(14) Pal, A.; Sharma, S. Excess Molar Volumes and Viscosities of Binary Liquid Mixtures of Ethylene Glycol Diethyl Ether + Ethylene Glycol Monomethyl, + Diethylene Glycol Monomethyl, and + Triethylene Glycol Monomethyl Ethers at 298.15 and 308.15 K. *J. Chem. Eng. Data* **1999**, *44*, 1067−1070.

(15) George, J.; Sastry, N. V. Densities, Excess Molar Volumes, Viscosities, Speeds of Sound, Excess Isentropic Compressibilities, and Relative Permittivities for $C_mH_{2m+1}(OCH_2CH_2)_nOH$ (m = 1 or 2 or 4 and n = 1) + Benzene, + Toluene, + (*o*-, *m*-, and *p*-) Xylenes, + Ethylbenzene, and + Cyclohexane. *J. Chem. Eng. Data* **2003**, *48*, 977−989.

(16) Tamura, K.; Osaki, A.; Murakami, S.; Laurent, B.; Grolier, J. P. Thermodynamic Properties of Binary Mixtures {x(2-alkoxyethanol) + (1-x) *n*-octane}: densities at 298.15 and 303.15 K and speeds of sound at 298.15 K. *Fluid Phase Equilib.* **2000**, *173*, 285−296.

(17) Pal, A.; Bhardwaj, R. K. Excess Molar Volumes and Viscosities for Binary Mixtures of 2-Propoxyethanol and of 2-Isopropoxyethanol with Propylamine and Dipropylamine at (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data* **2001**, *46*, 933−938.

(18) Pal, A.; Bhardwaj, R. K. Excess Molar Volumes and Viscosities for Binary Mixtures of 2-Propoxyethanol and of 2-Isopropoxyethanol with 2-Pyrrolidinone, *N*-Methyl-2-Pyrrolidinone, *N*,*N*-Dimethylformamide, and *N*,*N*-Dimethylacetamide at 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 1128−1134.

(19) Lagourette, B.; Boned, C.; Saint-Guirons, H.; Xans, P.; Zhou, H. Densimeter Calibration Method Versus Temperature and Pressure. *Meas. Sci. Technol.* **1992**, *3*, 699−703.

(20) Kell, G. S.; Whaley, E. J. Reanalysis of the density of liquid water in the range 0-150.deg. and 0-1 kbar. *J. Chem. Phys.* **1975**, *62*, 3496.

(21) Preston-Thomas, H. *Metrologia* **1990**, *27*, 3−10.

(22) McGlashan, M. L. The International Temperature Scale of 1990 (ITS-90). *J. Chem. Thermodyn.* **1990**, *22*, 653−663.

(23) Span, R. *Multiparameter Equations of State, An Accurate Source of Thermodynamic Property Data*; Springer: Berlin, 2000,

(24) Soave, G. Equilibrium Constants from a Modified Redlich-Kwong Equation of State. *Chem. Eng. Sci.* **1972**, *27*, 1197−1203.

(25) Péneloux, A.; Rauzy, E.; Freze, R. A Consistent Correction for Redlich-Kwong-Soave Volumes. *Fluid Phase Equilib.* **1982**, *8*, 7−23.

(26) Magoulas, K.; Tassios, D. Thermophysical Properties of *n*-Alkanes from C1 to C20 and their Prediction of Higher ones. *Fluid Phase Equilib.* **1990**, *56*, 116−140.
(27) Patel, N. C.; Teja, A. S. A New Cubic Equation of State for Fluids and Fluids Mixtures. *Chem. Eng. Sci.* **1982**, *37*, 463−473.
(28) Wilson, L. C.; Wilding, H. L.; Wilson, W. V.; Wilson, G. M. Critical Point Measurements for Fourteen Compounds by a Static Method and a Flow Method. *J. Chem. Eng. Data* **1996**, *41*, 1252−1254.
(29) Pick, J.; Fried, V.; Hala, E.; Vilim, O. Der Dampfdruck des Athylenglykolmonomethylathers und des Athylenglykolmonoathylathers. *Collect. Czech. Chem. Commun.* **1956**, *21*, 260−261.
(30) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986.
(31) Dykyj, J.; Seprakova, M.; Maulech, J. Physikalische Eigenschaften des Athylenglykols und Seiner Derivate (II) Dampftensionen von Alkoxyathanolen und Aneren Drivaten des Athylenglykols. *Chem. Zvesti* **1957**, *11*, 461−466.
(32) Lydersen, A. L. Estimation of critical properties of organic compounds by group contributions. *Univ. Wis. Coll. Eng. Exp. Sta. Rept.* **1955**, 7.
(33) Klincewicz, K. M.; Reid R. C. Estimation of critical properties with group contribution methods. *AIChE J.* **1984**, *30*, 137−142.

Received for review February 13, 2004. Accepted May 24, 2004.

JE049929F