Liquid Density Measurements of Diethylene Glycol Monoalkyl Ethers as a Function of Temperature and Pressure

Enriqueta R. López,[†] Luis Lugo,[†] María J. P. Comuñas,[†] Josefa García,[†,‡] 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 Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Vigo, E-36200 Vigo, Spain

In this work, 144 new experimental density values are reported for diethylene glycol monomethyl ether (DEGME) and diethylene glycol monoethyl ether (DEGEE) in the compressed liquid phase between 283.15 K and 353.15 K for pressures up to 25 MPa. The density measurements were performed with an Anton Paar DMA 60/512P vibrating tube densimeter and then correlated by using a Tammann−Tait equation with standard deviations of 1×10^{-4} $g\cdot cm^{-3}$. The isothermal compressibility, the isobaric thermal expansivity, and the internal pressure have been determined from the density data. The isothermal compressibility and isobaric thermal expansivity values increase with the size of the diethylene glycol monoalkyl ether molecule. The internal pressure values are lower for DEGEE than for DEGME.

Introduction

The reliable knowledge of the *pVT* behavior of pure compounds and mixtures is of great importance in many fields of research as well as in industrial practice. The densities of fluids as a function of temperature, pressure, and composition are particularly important for the design of industrial plants, pipelines, and pumps. These data are needed for solving material and energy balances required for the design and optimization of chemical processes. Furthermore, reliable density values are the basis for the development of correlation models and equations of state.

In this work, the volumetric behavior under pressure of two diethylene glycol monoalkyl ethers (Carbitols), which contain ethers and an alcohol group in the same molecule, has been studied. These compounds are miscible with a wide range of solvents including water. Due to their mild odor, glycol ethers are used as solvents for many resins, oils, waxes, fats, and dyestuffs. The product's ability to improve dye penetration makes it attractive for non-grain-raising wood stains, spirit-type dyes, and textile dye pastes. The glycol ethers are widely used as detergents by means of forming stable homogeneous solutions with high fractions of water and oil.[1,2] In addition, lubricants, hydraulic fluids, greases, and so forth contain glycol ethers, and also the compatibility of certain oil additives is improved and turbidity is corrected by addition of glycol ether type compounds such as diethylene glycol monoethyl ether. *pVT* data at medium and high pressures are needed for the simulation of the behavior of glycol ethers in real operation conditions for some applications. Despite these facts, literature density data for glycol ethers are scarce, and most of the values have been obtained at atmospheric pressure.

Our research concerning glycol ethers aims to create a complete database of pure fluids and their mixtures, which could be used for developing models to accurately represent the thermophysical properties of these compounds. The present work reports experimental density values and derived thermodynamic properties (isothermal compressibilities, isobaric thermal expansivities, and internal pressures) of diethylene glycol monomethyl ether (DEGME) and diethylene glycol monoethyl ether (DEGEE) in the temperature range from (283.15 to 353.15) K and at pressures up to 25 MPa.

Experimental Section

Materials. Diethylene glycol monomethyl ether (Aldrich, puriss, mole fraction purity of 0.99) and diethylene glycol monoethyl ether (Aldrich, puriss, mole fraction purity of >0.99) were used without purification except drying with Union Carbide 0.4 nm molecular sieves for several days. These chemicals and water (purified using a Milli-Q Plus system, with a resistivity of 18.2 MΩ·cm at 298.15 K) were partially degassed, before use, with a Branson 2210 ultrasonic bath.

Experimental Method. The Anton Paar DMA 60/512P vibrating tube densimeter was used to determine the experimental densities. This type of densimeter can be used to perform measurements from (263.15 to 423.15) K and up to 70 MPa but requires the construction and setup of several pieces of equipment and peripherals. A complete experimental assembly of the apparatus and the experimental procedure have been previously described in detail.[3,4]

The temperature inside the cell block was measured with an Anton Paar CKT100 platinum resistance thermometer with a resolution of ±0.001 K and an uncertainty of ±0.01 K due to its calibration. The pressure was measured by means of a HBM-PE300 differential pressure gauge, which can operate at pressures up to 50 MPa. This gauge was calibrated with an uncertainty of 0.02 MPa. In this work, the calibration parameters of the densimeter cell were determined using the more precise of the two calibration methods developed by Lagourette et al.[5] For this method, it is only necessary to know the density as a function of temperature and pressure for a reference fluid (water) and

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* To whom correspondence should be addressed. Tel: 34981563100 ext. 14046. Fax: 34981520676. E-mail: fajferna@usc.es.
[†] Universidad de Santiago de Compostela.
[‡] Universidad de Vigo.

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Table 1. Experimental Densities, ρ, for DEGME and DEGEE at Different Temperatures T and Pressures p

p	ρ/g·cm^{-3} at the following values of T/K							
MPa	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15
				DEGME				
0.10	1.0285	1.0195	1.0108	1.0020	0.9932	0.9839	0.9752	0.9657
1.00	1.0290	1.0200	1.0113	1.0026	0.9939	0.9846	0.9758	0.9664
2.50	1.0298	1.0209	1.0122	1.0035	0.9949	0.9856	0.9770	0.9676
5.00	1.0312	1.0223	1.0136	1.0051	0.9966	0.9874	0.9788	0.9695
7.50	1.0325	1.0237	1.0150	1.0067	0.9983	0.9891	0.9806	0.9714
10.00	1.0339	1.0252	1.0164	1.0082	1.0000	0.9908	0.9824	0.9733
15.00	1.0364	1.0279	1.0193	1.0112	1.0032	0.9941	0.9859	0.9769
20.00	1.0390	1.0305	1.0221	1.0141	1.0062	0.9972	0.9892	0.9804
25.00	1.0414	1.0331	1.0248	1.0169	1.0092	1.0002	0.9924	0.9837
				DEGEE				
0.10	0.9977	0.9884	0.9795	0.9706	0.9615	0.9524	0.9434	0.9341
1.00	0.9982	0.9889	0.9801	0.9712	0.9621	0.9531	0.9441	0.9349
2.50	0.9991	0.9898	0.9811	0.9722	0.9632	0.9543	0.9453	0.9361
5.00	1.0006	0.9913	0.9826	0.9739	0.9650	0.9561	0.9473	0.9382
7.50	1.0020	0.9928	0.9842	0.9755	0.9668	0.9580	0.9492	0.9402
10.00	1.0034	0.9943	0.9858	0.9771	0.9685	0.9597	0.9511	0.9422
15.00	1.0061	0.9972	0.9888	0.9803	0.9719	0.9632	0.9548	0.9460
20.00	1.0088	0.9999	0.9917	0.9834	0.9751	0.9665	0.9583	0.9497
25.00	1.0113	1.0026	0.9946	0.9863	0.9782	0.9698	0.9616	0.9532

also the temperature dependence of the period for the cell under vacuum. Taking into account the uncertainties in temperature, pressure, and the literature water density,[6] together with the reproducibility of the oscillation periods, an uncertainty of $\pm 10^{-4}$ g·cm^{-3} has been estimated.

Results and Discussion

Densities. Density measurements of DEGME and DEGEE were performed along eight isotherms between (283.15 and 353.15) K at 10 K intervals and along nine isobars at pressures up to 25 MPa. All experimental values are listed in Table 1.

The experimental ρpT values for DEGME and DEGEE were represented with the following modified Tammann–Tait equation:[7]

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

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

$$\rho(T, 0.1\ \mathrm{MPa}) = A_0 + A_1 T + A_2 T^2 + A_3 T^3 \qquad (2)$$

The A_i values were determined by smoothing the experimental densities at atmospheric pressure. The standard deviations, s, from these correlations are 1×10^{-4} g·cm^{-3} for DEGME and 0.9×10^{-4} g·cm^{-3} for DEGEE.

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

$$B(T) = B_0 + B_1 T + B_2 T^2 \qquad (3)$$

The values of B_i and C were determined by fitting all experimental data at elevated pressures to eq 1 using a Marquardt–Levenberg type algorithm.[8] The standard deviations, s^*, from the Tammann–Tait correlations are for both compounds 1×10^{-4} g·cm^{-3}. The set of the fitting coefficient (A_i, B_i, C) values and the standard deviations s and s^* are listed in Table 2.

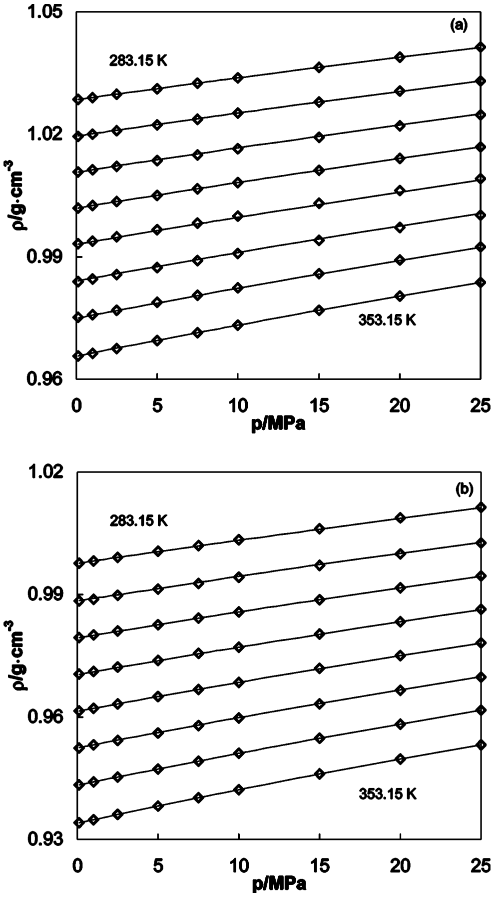

Figure 1. Experimental densities for (a) DEGME and (b) DEGEE versus pressure at different temperatures: ◇, experimental points (283.15, 293.15, 303.15, 313.15, 323.15, 333.15, 343.15, and 353.15) K; —, eq 1 with the parameters of Table 2.

Table 2. A_i, B_i, and C Coefficients and Standard Deviations, s and s^*, for Equations 1 and 2

	DEGME	DEGEE
A_0/g·cm^{-3}	1.54303	1.54496
$-A_1 \times 10^3$/g·cm^{-3}·K^{-1}	3.4848	3.6943
$A_2 \times 10^6$/g·cm^{-3}·K^{-2}	8.52	8.88
$-A_3 \times 10^9$/g·cm^{-3}·K^{-3}	9.3	9.4
$s \times 10^4$/g·cm^{-3}	1	0.9
B_0/MPa	672.7061	582.5406
$-B_1$/MPa·K^{-1}	2.6997	2.2909
$B_2 \times 10^3$/MPa·K^{-2}	3.033	2.511
C	0.080864	0.079588
$s^* \times 10^4$/g·cm^{-3}	1	1

The experimental density data together with the corresponding Tammann–Tait correlations are shown in Figure 1 for both glycol ethers. As usual, the values present increasing trends along isotherms and decreasing slopes at constant pressure, the density values of DEGEE being lower than those of DEGME. The function $B(T)$ decreases when the temperature rises and decreases with the increase of the CH$_2$ groups. The temperature dependence of $B(T)$ and its diminution when the number of CH$_2$ groups increases in the diethylene glycol monoalkyl ether molecule have also been found by other authors for other polar compounds such as polyalkylene glycol dimethyl ethers,[4] organic carbonates,[9] 2-alkanones,[10–12] and alkyl alkanoates.[13]

The comparison of our experimental values at atmospheric pressure at several temperatures with the literature data reported by several authors[14–22] gives an average absolute deviation (AAD) of 0.08% for DEGME and of 0.06% for DEGEE. Between the different literature data at atmospheric pressure, the deviations reach values of 0.4%.

At high pressure, only literature density values for DEGEE were found. Cibulka et al.[23] reported a set of parameters for the Tammann−Tait equation obtained from the experimental density data measured by Akhundov et al.[24] between (298.15 and 548.15) K and up to 25 MPa. Our experimental densities at pressures up to 25 MPa are always lower than those of Akhundov et al. presenting a very high AAD (about 3.4%). These discrepancies diminish slightly with an increase in pressure and increase at higher temperatures, showing a systematic deviation. The density values at 0.1 MPa reported by Akhundov et al. present an AAD of about 3.5% with several primary sources,[14,16,18−20] whereas our experimental data agree with the density values of these last references within an absolute average deviation of 0.06%. Furthermore, the experimental vapor pressures are reported for DEGEE by Akhundov et al.[24] between (498.15 and 548.15) K. These vapor pressure values are also in disagreement with the data obtained by Stull[25] between (318.4 and 475.0) K or with those determined by Gardner et al.[26] between (313.5 and 424.0) K. Perhaps the disagreement is due to the low purity of the samples used by Akhundov et al.

Derived Properties. Using the Tammann−Tait equation with the parameters presented in Table 2, the effects of both temperature and pressure on different thermophysical properties were evaluated.[3,4] The isothermal compressibility, $\kappa_T = (1/\rho)(\partial\rho/\partial p)_T$, and the isobaric thermal expansivity, $\alpha_p = -(1/\rho)(\partial\rho/\partial T)_p$, were determined. The estimated uncertainties of these properties are $\pm 0.03 \times 10^{-4}$ MPa^{-1} and $\pm 0.2 \times 10^{-4}$ K^{-1}, respectively.

The temperature dependence of the isothermal compressibilities, calculated from the Tammann−Tait equation, is determined mainly by the temperature dependence of the parameter $B(T)$ and is certainly the most direct way to obtain reliable isothermal compressibility values.[27] In Figure 2, the isothermal compressibility, κ_T, decreases when the pressure increases at constant temperature (about 13% and 14% at 323.15 K over the full pressure interval for DEGME and DEGEE, respectively) and rises with the temperature increases along isobars. The temperature and pressure trends for the isobaric thermal expansivity values are the same as for κ_T, that is, intersection or crossing points of isotherms were not found in the analyzed pT range.[9,28] Figure 3a shows the behavior of the isobaric thermal expansivity, α_p, as a function of pressure for DEGME and DEGEE at 323.15 K. Both magnitudes, α_p and κ_T, increase with the size of the diethylene glycol monoalkyl ether molecule.

Finally, the internal pressure, $\pi = T(\partial p/\partial T)_v - p = T(\alpha_p/k_T) - p$, was determined using the calculated values of isothermal compressibilities and isobaric thermal expansivities. The uncertainty is estimated to be less than 1 MPa over the full pressure and temperature ranges. The internal pressure values are quite large for these liquids. The values for DEGME are greater than those of DEGEE, ranging over all the temperature and pressure intervals from (413 to 450) MPa and from (388 to 434) MPa, respectively. The dipole moments[29] at 308.15 K for both glycol ethers are also high but very close, $\mu = 2.78$ D for DEGEE and $\mu = 2.75$ D for DEGME. This means that the insertion of a methylene group (nonpolar) reduces the internal pressure. This fact has also been observed previously for dialkyl carbonates,[9] 2-alkanones[11,12] (from 2-butanone to 2-hexanone), and ethyl alkanoates.[11−13]

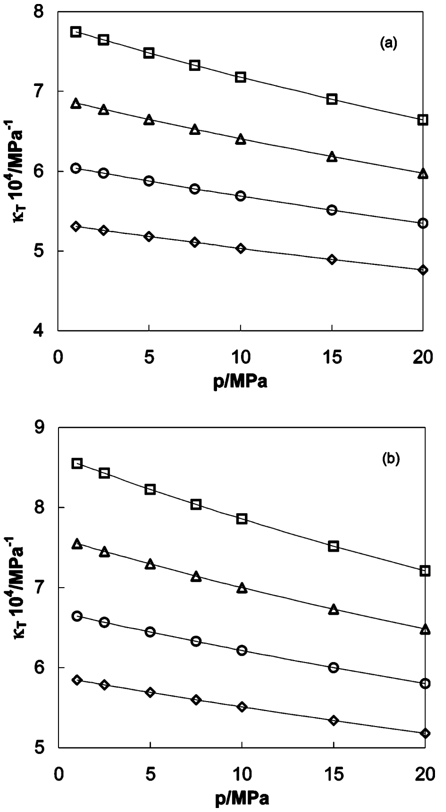

Figure 2. Isothermal compressibility, κ_T, as a function of pressure, p, at different temperatures, T: ◇, 283.15 K; ○, 303.15 K; △, 323.15 K; □, 343.15 K. (a) DEGME and (b) DEGEE.

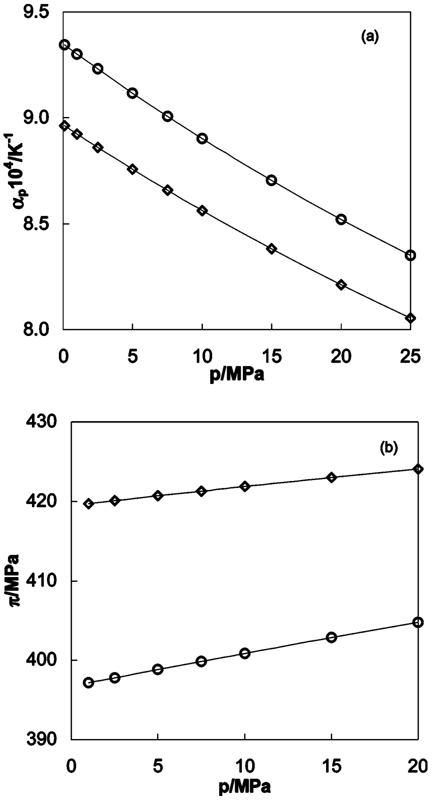

Figure 3. (a) Isobaric thermal expansivity, α_p, as a function of pressure, p, at $T = 323.15$ K. (b) Internal pressure, π, against the pressure at 323.15 K. ◇, DEGME; ○, DEGEE.

For both diethylene glycol monoalkyl ethers, the internal pressure increases along an isotherm when the pressure increases. This increase is 1% for DEGME and 2% for

DEGEE at 323.15 K, as shown in Figure 3b where plots of the internal pressure versus the pressure are shown. The values of the internal pressure for these pure liquids decrease with increase in temperature, or in other words, cohesive forces[30] decrease with temperature increase.

Conclusions

Densities of DEGME and DEGEE in the temperature range from (283.15 to 353.15) K and at pressures up to 25 MPa have been reported. Our experimental values have been compared with the available literature data at atmospheric pressure.[14−22,24] An AAD lower than or equal to 0.08% was found. For high pressures, the literature data reported by Akhundov et al.[24] for DEGEE have been analyzed and a high AAD (3.4%) with the experimental data of the present work was found. Systematic deviations between the atmospheric values of Akhundov et al.[24] and those reported by other authors were also observed. In this article, the parameter values for the Tammann−Tait equation for DEGEE have been revised and provided.

The isothermal compressibility and the isobaric thermal expansivity values increase with the size of the diethylene glycol monoalkyl ether molecule. The internal pressure values of DEGME are greater than those of DEGEE. It is hoped that the data will aid in testing models and equations of state in glycol ethers.

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