

Thermophysical Properties of Two Poly(alkylene glycol) Derivative Lubricants from High Pressure Acoustic Measurements

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The speeds of sound in two poly(alkylene glycol) derivatives (triethylene glycol dimethyl ether and tetraethylene glycol dimethyl ether) were measured, at temperatures from 293.15 to 353.15 K and pressures from atmospheric up to 100 MPa, using a pulse technique operating at 3 MHz, with an estimated error of less than $\pm 0.2\%$. From these measurements, and using literature density and heat capacity data at 0.1 MPa and at several temperatures, *PVT* surface and isentropic and isothermal compressibilities of each compound were estimated in the same experimental ranges of pressure and temperature.

Introduction

The knowledge of accurate thermophysical properties of organic fluids as a function of pressure and temperature is of essential importance in both the fundamental point of view and the applied one, in both science and technology fields.^{1–3} In this sense, one powerful thermophysical property is the speed of sound, which can be determined by highly accurate and simple experimental techniques in broad ranges of pressure and temperature.

Moreover, measurements of speed of sound in liquids at high pressures provide an easy and precise method for obtaining fundamental thermodynamic information of the fluid under investigation.^{4,5} Thus, from the speed of sound, the *PVT* surface and both isentropic and isothermal compressibilities at elevated pressures can be obtained if density and isobaric heat capacity are known along one isobar. Additionally, speed of sound data provide an essential consistency test in the development of precise equations of state.

On the other hand, throughout the years, mineral oils have been used in refrigeration systems for several areas of application such as industrial refrigeration, conditioned air, heat pumps, equipment of the home, or food distribution. Nevertheless, the traditional mineral oils are not compatible with new alternative refrigerants, and it is necessary to find new optimal lubricants.

These new oils offer advantages such as greater stability in the presence of coolants to high temperatures, better viscosity–temperature characteristics, and an optimal lubricity in the presence of refrigerants. These synthetic lubricant types are poly(α -olefins) (PAOs), alkylbenzenes (ABs), poly(alkylene glycols) or polyglycols (PAGs or PGs), and diesters (DEs). Among them, in recent years, investigations concerning PAGs are increasing because PAGs seem to be promising lubricants for the new alternative refrigerants of HFC type⁶ because of their adequate properties, such as good thermal and oxidative stability to high temperatures, high viscosity index, excellent lubricity,

high flash point, and low vapor pressure. PAGs can be used in broad ranges of temperatures and are unique among synthetic lubricants because of their high oxygen content, they are biodegradable, and in addition, their cleanliness, especially their low tendency to form carbon deposits, is extremely important. They are used in compressors with refrigerant type hydrocarbons like propane, inert gases, or tetrafluoroethane.

A lubricant can be subjected to a wide range of operating temperatures and pressures depending on the industrial application; therefore, to determine if a fluid would be an appropriate lubricant component, it is necessary to have a precise knowledge of its physical properties, such as density, elastic constants, and viscosity coefficients under pressure and temperature.

In this work we present several thermophysical properties (speed of sound, density, isothermal and isentropic compressibilities) determined from acoustic measurements on two PAG derivatives in the range of temperature from 293.15 K to 353.15 K and up to 100 MPa. The investigated compounds, corresponding to the general chemical formula $C_{2n+2}H_{4n+6}O_{n+1}$, were triethylene glycol dimethyl ether (TrEGDME, triglyme, $n = 3$) and tetraethylene glycol dimethyl ether (TEGDME, tetraglyme, $n = 4$). We must point out that although, from the chemical point of view, these compounds are not strictly poly(alkylene glycols) because they have no OH groups, for refrigeration engineering applications they are considering as PAG derivatives. Thus, Tsergounis and Riley⁷ have shown that the polyether compounds obtained by eliminating the terminal alcohol groups from glycol compounds have better properties as lubricants than the PAGs properly, due to the major affinity for the refrigerant molecules and the biggest solubilities of the HFCs in the polyethers.

Experimental Section

The measurements of the ultrasonic speed were carried out using a fixed path pulse echo technique. The apparatus, which has been described previously,⁸ consists essentially of a high-pressure cell made up of a stainless steel hollow cylinder closed at each extremity by plugs. A piezoelectric element (PZT) of natural frequency 3 MHz is mounted by

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means of a backing system on the external surface of each plug which acts as a buffer rod. A high voltage pulser-receiver (PANAMETRICS brand) is used to deliver a short pulse to the first transducer, which changes it into an ultrasonic wave. After propagating through the plugs and the fluid under investigation, the wave is converted by the second transducer into an electric signal, which is amplified and displayed on a numerical oscilloscope (GOULD brand) triggered by the pulse generator. The delay time is measured with an error of ± 5 ns by direct chronometry using the time base of the oscilloscope.⁹ This technique is capable of great precision in the measurement of the time delay. However, the ultimate accuracy of the ultrasonic speed depends on the precision of the determination of the path length L of the specimen between plugs. This length was determined by calibrating with water^{10–12} and was correlated to the temperature and pressure according to the following relation:

$$L(P, T) = L_0[1 + a(T - T_0)][1 + b(P - P_0)] \quad (1)$$

where T_0 and P_0 correspond respectively to the standard temperature and pressure and L_0 , a , and b are apparatus coefficients.

To ensure satisfactory thermal uniformity within the fluid, the cell is fully immersed in a bath of heat-carrying fluid agitated and thermoregulated by a thermostat (Bio-block brand) of stability 0.02 K over the temperature range (293 to 353 K). The temperature is monitored by a Pt100 probe placed inside the autoclave cell. The fluid is pressurized in a buffer tank made up of a stainless steel autoclave cylinder in which a mobile piston can move in such a way as to transfer the pressure to the fluid studied from the compression oil. The oil pressure is generated by a high-pressure pneumatic pump (Haskel brand). The pressure is measured between the cell and buffer tank using a transducer (HBM brand) which provides a voltage proportional to the pressure. This transducer was calibrated by a dead weight tester (Bundenberg brand) to an uncertainty of 0.02% at the higher pressure.

The technique used for evaluating the time delay as well as the specimen path length leads to an accuracy in the ultrasonic speed of about $\pm 0.06\%$. However, the ultimate precision depends also on the measurements of temperature (which causes an error in c of about $\pm 0.03\%$) and of pressure (which leads to an error in c of $\pm 0.1\%$ at most). This accuracy has been confirmed by several tests performed with hexane¹³ and heptane.¹⁴

The triethylene glycol dimethyl ether (molar mass: 178.229 g·mol⁻¹) and tetraethylene glycol dimethyl ether (molar mass: 222.282 g·mol⁻¹) were supplied by Aldrich with a mass fraction purity higher than 0.99 and were used without further purification.

Results and Discussion

The ultrasonic speed measurements were performed along isotherms spaced at 10 K intervals from (293.15 to 353.15) K in the pressure range from atmospheric pressure to 100 MPa using 10 MPa steps. The results are listed in Table 1, and some isobaric and isothermal curves are plotted in Figures 1 and 2, respectively. It can be observed that, along the isobaric curves, the speeds of sound have a linear decreasing trend, which is the usual behavior for liquids. Increasing the pressure produces a decrease of the slope of these curves. Similarly, a classical trend can be seen along the isothermal curves, where the ultrasonic speed values increase regularly with pressure.

Table 1. Speed of Sound, c , in the Liquids Triethylene Glycol Dimethyl Ether and Tetraethylene Glycol Dimethyl Ether at the Given Temperatures, T , and Pressures, P

| P/MPa | $c/\text{m}\cdot\text{s}^{-1}$ at the following values of T/K | | | | | | |
|----------------|--|--------|--------|--------|--------|--------|--------|
| | 293.15 | 303.15 | 313.15 | 323.15 | 333.15 | 343.15 | 353.15 |
| TrEGDME | | | | | | | |
| 0.1 | 1361.9 | 1323.2 | 1285.1 | 1247.7 | 1210.9 | 1174.6 | 1138.7 |
| 10 | 1403.1 | 1366.5 | 1330.0 | 1294.6 | 1259.5 | 1225.1 | 1191.5 |
| 20 | 1442.5 | 1407.2 | 1372.2 | 1338.5 | 1304.8 | 1272.0 | 1240.0 |
| 30 | 1479.3 | 1445.2 | 1411.8 | 1379.1 | 1346.9 | 1315.6 | 1284.6 |
| 40 | 1514.7 | 1481.6 | 1448.8 | 1417.3 | 1386.3 | 1356.2 | 1326.2 |
| 50 | 1547.8 | 1515.7 | 1484.1 | 1453.6 | 1423.4 | 1394.1 | 1365.6 |
| 60 | 1579.5 | 1548.2 | 1517.5 | 1487.9 | 1458.8 | 1430.3 | 1402.4 |
| 70 | 1610.0 | 1579.4 | 1549.7 | 1520.7 | 1492.1 | 1464.6 | 1437.6 |
| 80 | 1639.3 | 1609.3 | 1580.3 | 1552.0 | 1524.3 | 1497.2 | 1470.9 |
| 90 | 1667.4 | 1638.2 | 1609.9 | 1581.9 | 1554.8 | 1528.4 | 1502.6 |
| 100 | 1694.6 | 1665.9 | 1638.1 | 1610.8 | 1584.3 | 1558.5 | 1533.4 |
| TEGDME | | | | | | | |
| 0.1 | 1400.2 | 1361.6 | 1324.5 | 1288.0 | 1252.0 | 1216.6 | 1181.6 |
| 10 | 1439.3 | 1402.8 | 1367.0 | 1332.1 | 1297.9 | 1264.2 | 1231.2 |
| 20 | 1477.3 | 1441.7 | 1407.3 | 1373.8 | 1340.7 | 1308.6 | 1276.9 |
| 30 | 1512.3 | 1478.2 | 1444.9 | 1412.5 | 1380.8 | 1349.9 | 1319.8 |
| 40 | 1546.2 | 1513.0 | 1480.9 | 1449.5 | 1418.3 | 1388.8 | 1359.8 |
| 50 | 1578.2 | 1546.1 | 1514.8 | 1484.2 | 1454.2 | 1425.3 | 1397.1 |
| 60 | 1609.1 | 1577.7 | 1547.2 | 1517.4 | 1488.4 | 1460.1 | 1432.8 |
| 70 | 1638.4 | 1607.6 | 1578.1 | 1548.8 | 1520.7 | 1493.1 | 1466.5 |
| 80 | 1666.8 | 1637.0 | 1607.8 | 1579.3 | 1551.9 | 1524.7 | 1498.9 |
| 90 | 1694.2 | 1664.9 | 1636.4 | 1608.6 | 1581.5 | 1555.3 | 1529.8 |
| 100 | 1720.6 | 1692.0 | 1663.9 | 1636.7 | 1610.2 | 1584.4 | 1559.5 |

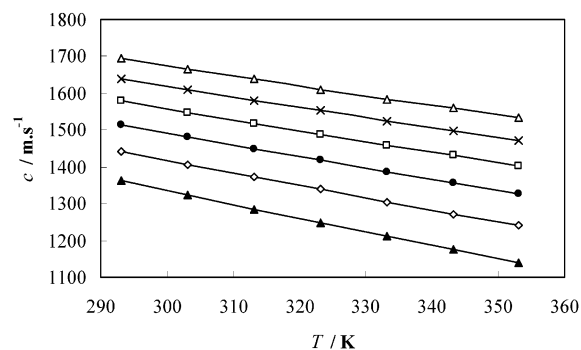


Figure 1. Speed of sound in triethylene glycol dimethyl ether as a function of temperature: \blacktriangle , $P = 0.1$ MPa; \diamond , $P = 20$ MPa; \bullet , $P = 40$ MPa; \square , $P = 60$ MPa; \times , $P = 80$ MPa; \triangle , $P = 100$ MPa.

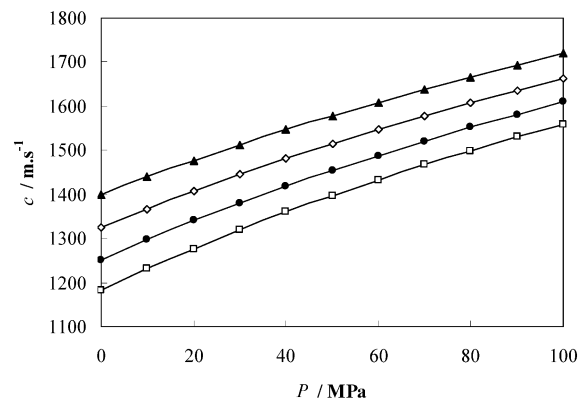


Figure 2. Speed of sound in tetraethylene glycol dimethyl ether as a function of pressure: \blacktriangle , $T = 293.15$ K; \diamond , $T = 313.15$ K; \bullet , $T = 333.15$ K; \square , $T = 353.15$ K.

The speed of sound was previously measured at atmospheric pressure, by Pereira et al.¹⁵ for triethylene glycol dimethyl ether and by Real et al.¹⁶ and Pereira et al.¹⁷ for tetraethylene glycol dimethyl ether. Comparison of our data interpolated at atmospheric pressure with a polynomial function of temperature with those reported by Pereira et

Table 2. Parameters of Eqs 5–7 with $c/\text{m}\cdot\text{s}^{-1}$, T/K , and P/MPa

| | TrEGDME | TEGDME |
|---------------------|------------------------------|------------------------------|
| A_0 | $-2.440\ 30 \times 10^{-7}$ | $1.158\ 98 \times 10^{-7}$ |
| A_1^1 | $3.575\ 86 \times 10^{-9}$ | $1.635\ 91 \times 10^{-10}$ |
| A_2 | $-8.725\ 80 \times 10^{-12}$ | $1.906\ 62 \times 10^{-12}$ |
| A_3 | $8.433\ 29 \times 10^{-15}$ | $-2.806\ 50 \times 10^{-15}$ |
| B | $1.158\ 69 \times 10^{-9}$ | $9.697\ 77 \times 10^{-10}$ |
| C | $-3.207\ 20 \times 10^{-12}$ | $-2.353\ 90 \times 10^{-12}$ |
| D | $7.268\ 02 \times 10^{-15}$ | $4.725\ 94 \times 10^{-15}$ |
| E_1 | $-1.723\ 61 \times 10^{-3}$ | $-1.693\ 89 \times 10^{-3}$ |
| F | $5.325\ 92 \times 10^{-3}$ | $4.884\ 92 \times 10^{-3}$ |
| AD ^a /% | 5.6×10^{-5} | -2.8×10^{-4} |
| AAD ^b /% | 1.2×10^{-2} | 9.2×10^{-3} |
| MD ^c /% | 4.4×10^{-2} | 3.0×10^{-2} |

^a AD = average deviation. ^b AAD = absolute average deviation. ^c MD = maximum deviation.

al.¹⁵ for triethylene glycol dimethyl ether shows good agreement with a maximum deviation of 0.1% between (293.15 and 308.15) K. A good concordance is also observed for tetraethylene glycol dimethyl ether with the data of Real et al.¹⁶ (with a maximum deviation of 0.05% between (293.15 and 308.15) K) and with the data of Pereira et al.¹⁷ (with a maximum deviation less than 0.08% up to 333.15 K).

Assuming that the dispersion of speed of sound with frequency is negligible between 0 and 3 MHz, the ultrasonic speed, assimilated with the speed of sound within the zero frequency limit c , can be correlated with various thermo-physical properties by means of isentropic, κ_S , and isothermal, κ_T , compressibilities:

$$\kappa_S = 1/\rho c^2 \quad (2)$$

$$\kappa_T = 1/\rho c^2 + T\alpha_P^2/\rho C_P \quad (3)$$

These relations enable, by integrating with respect to the pressure, to express the change in density versus pressure in terms of speed of sound:

$$\rho(P, T) - \rho(P_{\text{ref}}, T) = \int_{P_{\text{ref}}}^P 1/c^2 dP + T \int_{P_{\text{ref}}}^P (\alpha_P^2/C_P) dP \quad (4)$$

where α_P designates the isobaric coefficient of thermal expansion, C_P is the isobaric heat capacity, and P_{ref} is a reference pressure. To evaluate the first integral of eq 4, the sound speed data were smoothed as a function of temperature and pressure using a rational function which correlates directly $1/c^2$ as a function of pressure and temperature:

$$\frac{1}{c^2} = \frac{A + BP + CP^2 + DP^3}{E + FP} \quad (5)$$

in which

$$A = A_0 + A_1 T + A_2 T^2 + A_3 T^3 \quad (6)$$

and

$$E = 1 + E_1 T \quad (7)$$

The two sets of parameters determined by a least-squares method along with the average deviation, the average absolute deviation, and the maximum deviation are listed in Table 2. The maximum deviation observed between the experimental and calculated values shows that this function can be used to interpolate the speed of sound data of

Table 3. Parameters of Density, $\rho/\text{kg}\cdot\text{m}^{-3}$, and Heat Capacity, $C_p/\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$, Correlation Functions (with T/K) at Atmospheric Pressure

| | TrEGDME | TEGDME |
|----------|-----------------------------|-----------------------------|
| ρ_0 | $1.177\ 91 \times 10^{+3}$ | $1.267\ 02 \times 10^{+3}$ |
| ρ_1 | $-1.678\ 67 \times 10^{-1}$ | $-7.449\ 42 \times 10^{-1}$ |
| ρ_2 | $-2.345\ 96 \times 10^{-3}$ | $-6.753\ 80 \times 10^{-4}$ |
| ρ_3 | $2.314\ 73 \times 10^{-6}$ | $8.156\ 63 \times 10^{-7}$ |
| C_{p0} | $2.079\ 62 \times 10^{+3}$ | $2.818\ 31 \times 10^{+3}$ |
| C_{p1} | -1.494 58 | -5.589 30 |
| C_{p2} | $4.856\ 29 \times 10^{-3}$ | $1.018\ 46 \times 10^{-2}$ |

both components within the experimental accuracy. Moreover, comparisons of the average and average absolute deviations show that the smoothing function does not introduce any systematic error in the calculations. In addition, the random error contribution to experimental data becomes less significant by integration, and thus, the analytical integration of eq 5 leads to an accurate estimation of the first term of eq 4. The second integral of eq 4, which can be considered as a perturbation of the first one, is estimated iteratively using a predictor–corrector algorithm,⁸ which corresponds to a modification of the method proposed by Davis and Gordon.¹⁸ The atmospheric pressure density values required to initiate this iterative procedure were taken from literature data^{15–17,19–21} and were expressed as a cubic function of temperature in the temperature range investigated:

$$\rho_{\text{ref}} = \rho_0 + \rho_1 T + \rho_2 T^2 + \rho_3 T^3 \quad (8)$$

whereas the literature values of heat capacities at atmospheric pressure^{21–24} were fitted to a second-order polynomial function:

$$C_{p,\text{ref}} = C_{p0} + C_{p1} T + C_{p2} T^2 \quad (9)$$

The values of the fitted coefficients are given for both compounds in Table 3.

The density data, determined up to 100 MPa by this method, are listed in Table 4. On the basis of a previous work on hexane as reference fluid,¹³ it is estimated that the accuracy of these density data is better than $\pm 0.1\%$ in the whole experimental range. The present densities were compared with those due to Comuñas et al.,¹⁹ measured up to 60 MPa. An absolute average deviation of ($5 \times 10^{-3}\%$) and a maximum deviation of ($1.6 \times 10^{-2}\%$) were observed for TrEGDME. The comparison also reveals an excellent agreement between the two sets of data for TEGDME (average deviation of ($4.7 \times 10^{-3}\%$), maximum deviation ($1.9 \times 10^{-2}\%$)). Moreover, it can be noted from Figure 3 that the deviations do not increase systematically with pressure. The knowledge of c and ρ at the same conditions makes it possible to plot a set of curves $c(\rho)$ along isobars and isotherms (Figure 4). It can be seen that the isobaric as well as the isothermal curves have a linear trend, which is a classical trend of the liquid state.

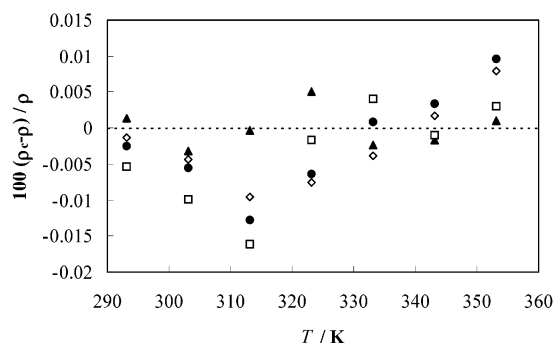
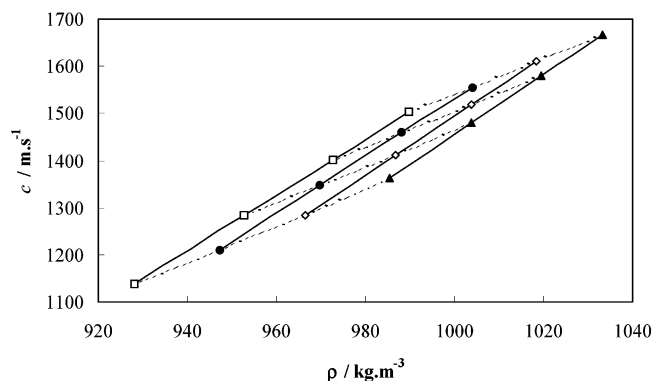
Finally, as the procedure rests on the link between the speed of sound and compressibilities, it can be used to evaluate the isentropic and isothermal compressibilities with an uncertainty less than $\pm 0.3\%$ and $\pm 2\%$, respectively. The values of these derived properties for TrEGDME and TEGDME are gathered in Tables 5 and 6.

The P – ρ – T data were fitted to a Tait-like equation:

$$\frac{1}{\rho} - \frac{1}{\rho_0} = a \ln\left(\frac{P+b}{P_0+b}\right) \quad (10)$$

Table 4. Densities, ρ , of the Liquids Triethylene Glycol Dimethyl Ether and Tetraethylene Glycol Dimethyl Ether at the Given Temperatures, T , and Pressures, P

| P/MPa | $\rho/\text{kg}\cdot\text{m}^{-3}$ at the following values of T/K | | | | | | |
|----------------|--|---------|---------|---------|---------|---------|---------|
| | 293.15 | 303.15 | 313.15 | 323.15 | 333.15 | 343.15 | 353.15 |
| TrEGDME | | | | | | | |
| 0.1 | 985.41 | 975.92 | 966.38 | 956.80 | 947.20 | 937.60 | 928.00 |
| 10 | 991.85 | 982.71 | 973.55 | 964.37 | 955.20 | 946.05 | 936.94 |
| 20 | 997.96 | 989.14 | 980.30 | 971.47 | 962.66 | 953.89 | 945.19 |
| 30 | 1003.73 | 995.19 | 986.64 | 978.11 | 969.61 | 961.17 | 952.81 |
| 40 | 1009.21 | 1000.92 | 992.62 | 984.35 | 976.12 | 967.96 | 959.90 |
| 50 | 1014.44 | 1006.36 | 998.29 | 990.25 | 982.26 | 974.35 | 966.56 |
| 60 | 1019.43 | 1011.55 | 1003.68 | 995.85 | 988.08 | 980.39 | 972.83 |
| 70 | 1024.22 | 1016.52 | 1008.83 | 1001.19 | 993.61 | 986.12 | 978.76 |
| 80 | 1028.82 | 1021.29 | 1013.77 | 1006.29 | 998.89 | 991.59 | 984.41 |
| 90 | 1033.25 | 1025.87 | 1018.51 | 1011.19 | 1003.95 | 996.80 | 989.80 |
| 100 | 1037.53 | 1030.29 | 1023.07 | 1015.90 | 1008.80 | 1001.81 | 994.96 |
| TEGDME | | | | | | | |
| 0.1 | 1011.15 | 1001.85 | 992.56 | 983.29 | 974.04 | 964.82 | 955.64 |
| 10 | 1017.21 | 1008.23 | 999.28 | 990.36 | 981.49 | 972.66 | 963.88 |
| 20 | 1023.00 | 1014.30 | 1005.64 | 997.03 | 988.48 | 979.98 | 971.56 |
| 30 | 1028.48 | 1020.04 | 1011.64 | 1003.30 | 995.02 | 986.82 | 978.70 |
| 40 | 1033.71 | 1025.48 | 1017.32 | 1009.21 | 1001.18 | 993.23 | 985.38 |
| 50 | 1038.70 | 1030.68 | 1022.72 | 1014.83 | 1007.02 | 999.29 | 991.67 |
| 60 | 1043.48 | 1035.64 | 1027.87 | 1020.18 | 1012.56 | 1005.04 | 997.62 |
| 70 | 1048.08 | 1040.41 | 1032.81 | 1025.29 | 1017.85 | 1010.51 | 1003.28 |
| 80 | 1052.50 | 1044.99 | 1037.55 | 1030.19 | 1022.91 | 1015.74 | 1008.67 |
| 90 | 1056.77 | 1049.40 | 1042.11 | 1034.89 | 1027.77 | 1020.74 | 1013.83 |
| 100 | 1060.90 | 1053.66 | 1046.50 | 1039.42 | 1032.44 | 1025.55 | 1018.78 |

**Figure 3.** Deviations (%) between the densities ρ deduced from acoustic measurements and those of Comuñas et al.¹⁹ ρ_c for several isobars: \blacktriangle , $P = 0.1$ MPa; \diamond , $P = 20$ MPa; \bullet , $P = 40$ MPa; \square , $P = 60$ MPa.**Figure 4.** Speed of sound of tetraethylene glycol dimethyl ether versus density: ---, along isobars; —, along isotherms (\blacktriangle , $T = 293.15$ K; \diamond , $T = 313.15$ K; \bullet , $T = 333.15$ K; \square , $T = 353.15$ K).

where ρ_0 is defined by eq 8, P_0 is the atmospheric pressure (0.1013 MPa), and the a and b parameters are expressed as a function of temperature using a second-order polynomial function:

$$a = a_0 + a_1 T + a_2 T^2 \quad (11)$$

Table 5. Isentropic Compressibility, κ_S , of the Liquids Triethylene Glycol Dimethyl Ether and Tetraethylene Glycol Dimethyl Ether at the Given Temperatures, T , and Pressures, P

| P/MPa | κ_S/GPa^{-1} at the following values of T/K | | | | | | |
|----------------|--|--------|--------|--------|--------|--------|--------|
| | 293.15 | 303.15 | 313.15 | 323.15 | 333.15 | 343.15 | 353.15 |
| TrEGDME | | | | | | | |
| 0.1 | 0.5471 | 0.5852 | 0.6266 | 0.6714 | 0.7200 | 0.7730 | 0.8310 |
| 10 | 0.5121 | 0.5450 | 0.5806 | 0.6187 | 0.6599 | 0.7043 | 0.7519 |
| 20 | 0.4816 | 0.5106 | 0.5418 | 0.5746 | 0.6101 | 0.6479 | 0.6881 |
| 30 | 0.4552 | 0.4811 | 0.5085 | 0.5376 | 0.5685 | 0.6011 | 0.6360 |
| 40 | 0.4319 | 0.4552 | 0.4799 | 0.5057 | 0.5330 | 0.5617 | 0.5923 |
| 50 | 0.4115 | 0.4325 | 0.4548 | 0.4779 | 0.5025 | 0.5280 | 0.5548 |
| 60 | 0.3932 | 0.4124 | 0.4326 | 0.4536 | 0.4756 | 0.4986 | 0.5227 |
| 70 | 0.3767 | 0.3944 | 0.4127 | 0.4319 | 0.4520 | 0.4727 | 0.4944 |
| 80 | 0.3617 | 0.3781 | 0.3950 | 0.4126 | 0.4309 | 0.4499 | 0.4695 |
| 90 | 0.3481 | 0.3632 | 0.3788 | 0.3952 | 0.4121 | 0.4295 | 0.4475 |
| 100 | 0.3356 | 0.3497 | 0.3643 | 0.3794 | 0.3949 | 0.4110 | 0.4274 |
| TEGDME | | | | | | | |
| 0.1 | 0.5044 | 0.5384 | 0.5743 | 0.6131 | 0.6550 | 0.7003 | 0.7494 |
| 10 | 0.4746 | 0.5041 | 0.5355 | 0.5690 | 0.6049 | 0.6433 | 0.6844 |
| 20 | 0.4479 | 0.4744 | 0.5021 | 0.5314 | 0.5628 | 0.5959 | 0.6312 |
| 30 | 0.4251 | 0.4487 | 0.4735 | 0.4996 | 0.5271 | 0.5561 | 0.5866 |
| 40 | 0.4047 | 0.4260 | 0.4482 | 0.4716 | 0.4966 | 0.5220 | 0.5489 |
| 50 | 0.3865 | 0.4059 | 0.4261 | 0.4473 | 0.4696 | 0.4926 | 0.5166 |
| 60 | 0.3701 | 0.3879 | 0.4064 | 0.4257 | 0.4458 | 0.4667 | 0.4883 |
| 70 | 0.3554 | 0.3719 | 0.3888 | 0.4066 | 0.4249 | 0.4439 | 0.4635 |
| 80 | 0.3420 | 0.3571 | 0.3728 | 0.3892 | 0.4059 | 0.4235 | 0.4413 |
| 90 | 0.3297 | 0.3438 | 0.3583 | 0.3734 | 0.3890 | 0.4050 | 0.4214 |
| 100 | 0.3184 | 0.3315 | 0.3452 | 0.3591 | 0.3736 | 0.3884 | 0.4036 |

$$b = b_0 + b_1 T + b_2 T^2 \quad (12)$$

The values of the parameters a_i and b_i ($i = 0, 1, 2$) as well as the average and maximum deviations are reported in Table 7 for both compounds. Examination of these deviations shows that this two-dimensional function can match the density data within the experimental error. Furthermore, this function was used to derive the isothermal compressibility. The comparison reveals excellent agreement between the two sets of compressibility data, those resulting from eq 3 on one hand and those resulting from the derivative of the Tait equation on the other hand. The two data sets deviate by a 0.2% average absolute deviation

Table 6. Isothermal Compressibility, κ_T , of the Liquids Triethylene Glycol Dimethyl Ether and Tetraethylene Glycol Dimethyl Ether at the Given Temperatures, T , and Pressures, P

| P/MPa | κ_T/GPa^{-1} at the following values of T/K | | | | | | |
|----------------|--|--------|--------|--------|--------|--------|--------|
| | 293.15 | 303.15 | 313.15 | 323.15 | 333.15 | 343.15 | 353.15 |
| TrEGDME | | | | | | | |
| 0.1 | 0.6805 | 0.7278 | 0.7786 | 0.8326 | 0.8905 | 0.9525 | 1.0193 |
| 10 | 0.6353 | 0.6749 | 0.7176 | 0.7629 | 0.8116 | 0.8636 | 0.9190 |
| 20 | 0.5950 | 0.6296 | 0.6666 | 0.7052 | 0.7468 | 0.7907 | 0.8371 |
| 30 | 0.5603 | 0.5909 | 0.6231 | 0.6571 | 0.6929 | 0.7305 | 0.7703 |
| 40 | 0.5298 | 0.5571 | 0.5860 | 0.6159 | 0.6473 | 0.6800 | 0.7147 |
| 50 | 0.5032 | 0.5277 | 0.5535 | 0.5801 | 0.6082 | 0.6371 | 0.6672 |
| 60 | 0.4794 | 0.5017 | 0.5250 | 0.5489 | 0.5738 | 0.5997 | 0.6266 |
| 70 | 0.4580 | 0.4784 | 0.4995 | 0.5212 | 0.5439 | 0.5670 | 0.5910 |
| 80 | 0.4387 | 0.4575 | 0.4767 | 0.4966 | 0.5171 | 0.5382 | 0.5599 |
| 90 | 0.4212 | 0.4385 | 0.4562 | 0.4745 | 0.4933 | 0.5126 | 0.5323 |
| 100 | 0.4053 | 0.4213 | 0.4377 | 0.4546 | 0.4718 | 0.4894 | 0.5074 |
| TEGDME | | | | | | | |
| 0.1 | 0.6239 | 0.6648 | 0.7078 | 0.7535 | 0.8023 | 0.8544 | 0.9103 |
| 10 | 0.5850 | 0.6199 | 0.6569 | 0.6960 | 0.7374 | 0.7814 | 0.8281 |
| 20 | 0.5501 | 0.5812 | 0.6135 | 0.6474 | 0.6833 | 0.7209 | 0.7606 |
| 30 | 0.5203 | 0.5478 | 0.5765 | 0.6064 | 0.6377 | 0.6703 | 0.7043 |
| 40 | 0.4937 | 0.5184 | 0.5440 | 0.5706 | 0.5987 | 0.6272 | 0.6569 |
| 50 | 0.4701 | 0.4925 | 0.5156 | 0.5396 | 0.5645 | 0.5901 | 0.6165 |
| 60 | 0.4490 | 0.4694 | 0.4904 | 0.5121 | 0.5345 | 0.5575 | 0.5811 |
| 70 | 0.4300 | 0.4488 | 0.4680 | 0.4879 | 0.5081 | 0.5290 | 0.5502 |
| 80 | 0.4128 | 0.4300 | 0.4477 | 0.4659 | 0.4844 | 0.5035 | 0.5227 |
| 90 | 0.3970 | 0.4130 | 0.4293 | 0.4461 | 0.4632 | 0.4805 | 0.4982 |
| 100 | 0.3826 | 0.3974 | 0.4127 | 0.4281 | 0.4439 | 0.4599 | 0.4761 |

Table 7. Parameters of the Tait Equation (Eqs. (10) – (12)) with $\rho/\text{kg}\cdot\text{m}^{-3}$, κ_T/GPa^{-1} , T/K and P/MPa

| | TrEGDME | TEGDME |
|---------------------------|-----------------------------|-----------------------------|
| a_0 | $-4.326\ 80 \times 10^{-6}$ | $-1.323\ 40 \times 10^{-5}$ |
| a_1 | $-4.502\ 60 \times 10^{-7}$ | $-3.827\ 00 \times 10^{-7}$ |
| a_2 | $5.563\ 79 \times 10^{-10}$ | $4.621\ 33 \times 10^{-10}$ |
| b_0 | $4.363\ 80 \times 10^{+2}$ | $4.763\ 71 \times 10^{+2}$ |
| b_1 | $-1.336\ 10$ | $-1.504\ 12$ |
| b_2 | $9.726\ 15 \times 10^{-4}$ | $1.207\ 03 \times 10^{-3}$ |
| $\text{AD}(\rho)/\%$ | -3.8×10^{-4} | -3.4×10^{-4} |
| $\text{AAD}(\rho)/\%$ | 1.8×10^{-3} | 1.5×10^{-3} |
| $\text{MD}(\rho)/\%$ | 5.7×10^{-3} | 4.2×10^{-3} |
| $\text{AD}(\kappa_T)/\%$ | 1.2×10^{-1} | 1.1×10^{-1} |
| $\text{AAD}(\kappa_T)/\%$ | 2.9×10^{-1} | 2.6×10^{-1} |
| $\text{MD}(\kappa_T)/\%$ | 8.7×10^{-1} | 8.0×10^{-1} |

and 0.9% at the maximum. The data of compressibility reported in Table 6 were compared with those due to Comuñas et al.,¹⁹ calculated by direct derivation of density data between 5 and 55 MPa in the temperature range (293 to 333) K. An absolute average deviation of 0.1% and a maximum deviation of 0.3% were observed for both compounds. These values reveal an excellent agreement between the two procedures of determination of this derived property.

Conclusions

Several thermophysical properties of TrEGDME and TEGDME, that is, speeds of sound, the PVT surface, and isothermal and isentropic compressibilities, have been determined from direct acoustic measurements in the ranges $293.15\ \text{K} \leq T \leq 353.15\ \text{K}$ and $0.1\ \text{MPa} \leq P \leq 100\ \text{MPa}$. In the case of densities and isothermal compressibilities, the comparison between the reported values and literature data determined by densimetry up to 60 MPa reveals an excellent concordance, concluding that the differences are closed to the uncertainties of both experimental methods.

In addition, several other thermophysical properties, namely the isobaric expansion, α_P , the heat capacity ratio,

γ , the isobaric, C_P , and isochoric, C_V , heat capacities, the enthalpy, H , and the entropy, S , can be evaluated as a function of pressure from the data of ρ , c , κ_S , and κ_T reported here, using the following relations:

$$\alpha_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \quad (13)$$

$$\gamma = \frac{\kappa_T}{\kappa_S} \quad (14)$$

$$\left(\frac{\partial C_P}{\partial P} \right)_T = -\frac{T}{\rho} \left(\alpha_P^2 + \left(\frac{\partial \alpha_P}{\partial T} \right)_P \right) \quad (15)$$

$$C_V = \frac{\kappa_S}{\kappa_T} C_P \quad (16)$$

$$\left(\frac{\partial H}{\partial P} \right)_T = -\frac{1}{\rho} (\alpha_P T - 1) \quad (17)$$

$$\left(\frac{\partial S}{\partial P} \right)_T = -\frac{\alpha_P}{\rho} \quad (18)$$

However, the calculation of these additional properties requires an accurate estimation of the derivative of density with respect to temperature to be valid.

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