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Temperature and Pressure Dependences of Thermophysical Properties of Some Ethylene Glycol Dimethyl Ethers from Ultrasonic Measurements

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In this work, the speed of sound was measured in monoglyme (monoethylene glycol dimethyl ether or MEGDME) and diglyme (diethylene glycol dimethyl ether or DEGDME) in the temperature range $293.15 \leqslant T/\mathrm{K} \leqslant 353.15$ at pressures up to 100 MPa using a pulse echo technique operating at 3 MHz; several thermophysical properties were determined in the same P-T range from these measurements. Furthermore, the density, isothermal compressibility, and isobaric thermal expansion coefficient, determined from volumetric data (direct method) and from acoustic measurements (indirect method) for four glymes have been compared. The comparison was extended to a second-order derivative of density with pressure, namely, the nonlinear acoustic parameter B/A.

KEY WORDS: compressibilities; density; diethylene glycol dimethyl ether; glymes; monoethylene glycol dimethyl ether; pressure; speed of sound.

1. INTRODUCTION

Due to quick changes in technology, new products and processes are necessary. The development and design of both products and processes for new clean industrial applications require the knowledge of several thermodynamic and thermophysical properties of fluids as functions of both temperature and pressure. With this aim in mind, the most valuable properties are density, viscosity, phase equilibria, and calorimetric properties.

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In this sense, ultrasonic techniques due to their simplicity and accuracy are recently being most applied in the study of the liquid state. In addition, the speed of sound is currently considered to be one of the most useful properties, due to its relationship with some volumetric and enthalpic properties and it can be used to calculate various thermoelastic coefficients [1, 2]. Furthermore, in recent years acoustic techniques have been used to determine other thermophysical properties such as the viscosity [3, 4].

Since most thermophysical properties are linked together by thermodynamic relations, only some of them have to be measured under pressure, the others being determined from these measured properties. In this sense, two approaches exist. First, the direct method consists of measuring the density and then calculating the other properties by differentiation with respect to temperature and pressure. Second, the inverse method, is based either on the integration of the isobaric thermal expansion coefficient with respect to temperature or on the integration of the isothermal compressibility with respect to pressure. The second approach seems to be more reliable as integrations are more accurate than numerical derivatives. Direct measurements of derived properties are nevertheless very difficult to perform accurately. In this respect, measurements of the speed of sound in liquids at high pressures provide an easy and precise method for obtaining compressibilities and thus other fundamental thermodynamic information of the studied fluid, if the density and isobaric heat capacity are known along one isobar.

Glymes are some of the most powerful solvents for a wide variety of industrial processes and products. Their unique properties play a vital role in many important applications. Glymes are saturated polyethers with no additional functional groups; hence, they are aprotic compounds that are relatively inert chemically. This all-ether structure produces associations between glyme molecules, which become weaker when the molecular size diminishes and are responsible for the low viscosity of these materials, especially monoglymes and diglymes, an important advantage in many applications, such as solvents for battery electrolytes. Glymes are also very powerful extracting agents. Due to their thermal stability, they are used in several high temperature applications.

Moreover, the high absorption capacity of ethylene glycol dimethyl ethers (a type of glyme) for gases makes these products ideal for use as a physical absorption medium. In relation to this property, absorption refrigeration is one of the most efficient systems to use residual thermal energy. In recent years, several ethylene glycol dimethyl ethers have been investigated as absorbents of natural and alternative refrigerants for absorption and absorption–compression systems [5–8]. Tetraglyme is also proposed as a lubricant for compression refrigeration systems using hydrofluorocarbons (HFCs) [9]. In summary, glymes are very useful functional fluids.

Due to the interest in these compounds, several thermophysical properties of different pure glymes and some of their mixtures with other compounds, over broad temperature and pressure ranges, were studied [10–14]. Following this research line in a previous study [15], the speed of sound in two glymes (triethylene glycol dimethyl ether, triglyme, or TrEGDME and tetraethylene glycol dimethyl ether, tetraglyme, or TEGDME) were reported from 293.15 to 353.15 K at pressures from atmospheric up to 100 MPa, together with density and isothermal and isentropic compressibilities. Subsequently, in this work the speed of sound in two other glymes, monoethylene glycol dimethyl ether (MEGDME, monoglyme) and diethylene glycol dimethyl ether (DEGDME, diglyme), have been measured in the temperature range from 283.15 to 353.15 K at pressures up to 100 MPa.

Based on the experimental data, several thermophysical properties, namely, density and isothermal and isentropic compressibilities, are reported for the same pressure and temperature ranges. Moreover, the variation of these and other properties (thermal expansion coefficient, acoustic impedance, or the acoustic nonlinear parameter B/A) with the chain length of the glymes have been analyzed.

2. EXPERIMENTAL

2.1. Materials

MEGDME (CAS 110-71-4, molar mass $90.122\,\mathrm{g \cdot mol^{-1}}$) and DEGDME (CAS 111-96-6, molar mass $134.175\,\mathrm{g \cdot mol^{-1}}$) were obtained from Aldrich with purities of 99.9% and 99.5%, respectively. These chemicals were subjected to no further purification.

2.2. Procedure

Speed-of-sound measurements were carried out using a pulse echo technique operating at 3 MHz. The main part of the experimental apparatus, which has been described in a previous publication [16], consists of a hollow cylinder closed at both ends by two piezoelectric transducers with the same resonance frequency. These transducers are connected to an ultrasonic emission/reception device (Panametrics 5055 PRM), which allows measurements by transmission and reflection. The speed of sound is deduced from a double measurement by transmission and by reflection of the transit time of the wave through the sample [17] using a digital oscilloscope with memory storage (Gould 4090). The length of the sample path was determined precisely by calibration with water using the data of Del Grosso and Mader [18], Wilson [19], and Petitet et al. [20]. The temperature is controlled by a thermostat with a stability of 0.02 K, and temperature measurements are carried out using a calibrated platinum resistance placed inside the experimental vessel. The pressure is generated by a pneumatic pump (Haskel) and measured by an HBM P3M gauge, which is frequently checked against a dead-weight tester (Bundenberg) to an uncertainty of better than 0.02%. Several tests performed with hexane [21] have shown that an overall uncertainty of less than 0.2% is obtained over the entire pressure range of 0.1–100 MPa.

3. RESULTS AND DISCUSSION

The ultrasonic speed measurements for both glymes were performed along isotherms from 293.15 to 353.15 K in the pressure range from atmospheric pressure up to 100 MPa. The results are presented in Table I, and are plotted as functions of pressure and temperature in Figs. 1 and 2. It can be observed that along isobaric curves, the speeds of sound have a linear decreasing trend, which is the usual behavior for liquids. An increase of the pressure produces a decrease of the slope of these curves (Fig. 1). Similarly, the classical trend can be seen in Fig. 2 along the isothermal curves, where the ultrasonic speed values increase regularly with pressure.

Comparisons of our experimental sound-speed data at atmospheric pressure with literature data were performed for both compounds. In the case of MEGDME, the deviation between our data point at 298.15 K and the value reported by Pal et al. [22] is 0.11%; at this same temperature the difference with the value published by Douheret et al. [23] is 0.07%. For DEGDME (Fig. 3) at 298.15 K, our result agrees with the value reported by Pal et al. [22] (0.04%) and with that due to Douheret et al. [23] (-0.03%). Nevertheless, comparisons of our data with those reported by Aminabhavi et al. [24] show poor agreement, with a maximum deviation of 0.79% at 318.15 K and an average absolute deviation (AAD) of 0.59% between 298.15 and 318.15 K. Comparison of our data between 298.15 and 318.15 K with other data of Aminabhavi et al. [25] shows a maximum deviation of 0.87% at 308.15 K and an average absolute deviation of 0.57%. We must point out that, at 298.15 K, the Aminabhavi et al. data [24, 25] also do not agree with those of Pal et al. [22] and of Douheret et al. [23], showing deviations of −0.74 and −0.35%, respectively, i.e., the data of Aminabhavi et al. [24, 25] are always higher.

Assuming that the dispersion of speed of sound with frequency is negligible between zero and 3 MHz, the ultrasonic speed (a mechanical

Table I. Speed of Sound c in Liquid Monoethylene Glycol Dimethyl Ether (MEGDME) and Diethylene Glycol Dimethyl Ether (DEGDME) at Temperature T and Pressure P

	T (K)						
	293.15	303.15	313.15	323.15	333.15	343.15	353.15
P(MPa)	c $(\mathrm{m \cdot s^{-1}})$						
MEGDME							
0.1	1188.5	1144.8	1101.9	1059.4	1016.5	974.9	932.8
10	1242.0	1201.1	1161.1	1122.4	1083.1	1044.7	1005.8
20	1292.4	1252.2	1215.2	1178.7	1142.7	1107.0	1070.0
30	1336.4	1299.6	1263.9	1229.3	1195.2	1161.4	1127.3
40	1378.8	1343.2	1309.2	1275.9	1243.6	1211.6	1178.9
50	1418.2	1384.1	1350.7	1319.6	1288.4	1257.6	1226.3
60	1455.6	1422.5	1390.5	1361.5	1330.1	1300.5	1270.4
70	1490.4	1458.0	1428.3	1398.6	1369.3	1340.5	1311.3
80	1523.9	1492.6	1463.3	1434.7	1406.4	1378.6	1350.2
90	1555.7	1525.7	1497.0	1468.9	1441.3	1414.5	1387.0
100	1586.1	1557.2	1528.8	1501.5	1474.8	1448.7	1421.7
DEGDME							
0.1	1298.9	1259.3	1219.9	1180.9	1142.4	1104.2	1066.6
10	1344.9	1306.7	1269.5	1232.5	1196.4	1160.8	1125.7
20	1386.5	1350.6	1315.4	1280.2	1246.0	1212.0	1179.3
30	1426.6	1392.0	1357.6	1324.4	1291.4	1259.5	1228.1
40	1463.9	1430.4	1397.8	1365.5	1333.7	1303.1	1273.4
50	1499.2	1466.9	1435.3	1404.0	1373.6	1343.9	1314.9
60	1532.5	1501.5	1470.5	1440.6	1410.9	1382.1	1354.4
70	1565.1	1534.3	1504.4	1475.2	1446.2	1418.6	1391.3
80	1595.5	1565.8	1536.7	1508.2	1480.1	1452.9	1426.7
90	1624.9	1595.9	1567.6	1539.8	1512.3	1485.9	1460.4
100	1653.4	1625.1	1597.0	1569.9	1543.1	1517.4	1492.3

property of a fluid), assimilated with the speed of sound within the zero frequency limit c, is linked to thermodynamics by the isentropic compressibility. Consequently, the speed of sound can be related with various thermophysical properties by means of isoentropic, κ_S, and isothermal, κ_T, compressibilities:

$$\kappa_S = 1/\left(\rho c^2\right), \tag{1}$$

$$\kappa_T = 1/\left(\rho c^2\right) + T\alpha_P^2/(\rho C_P), \tag{2}$$

where ρ designates the density, α_P is the isobaric thermal expansion coefficient, and C_P is the isobaric heat capacity.

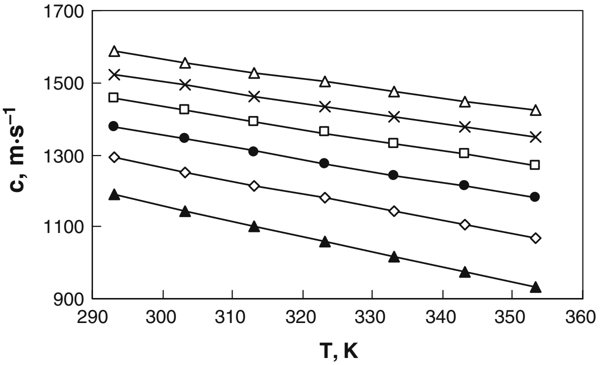

Fig. 1. Speed of sound in monoethylene glycol dimethyl ether as a function of temperature. ▲, $P = 0.1$ MPa; ◇, $P = 20$ MPa; ●, $P = 40$ MPa; □, $P = 60$ MPa; ×, $P = 80$ MPa; △, $P = 100$ MPa.

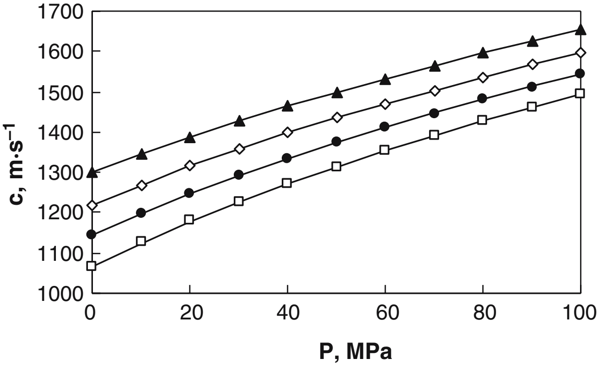

Fig. 2. Speed of sound in DEGDME as a function of pressure. ▲, $T = 293.15$ K; ◇, $T = 313.15$ K; ●, $T = 333.15$ K; □, $T = 353.15$ K.

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

$$\rho(P,T) - \rho(P_{\text{ref}},T) = \int_{P_{\text{ref}}}^{P} 1/c^2\,dP + T\int_{P_{\text{ref}}}^{P} (\alpha_P{}^2/C_P)\,dP \tag{3}$$

where P_{ref} is a reference pressure. In order to evaluate the first integral of Eq. (3), the sound-speed data were smoothed as a function of temperature and pressure using the following rational function, which correlates $1/c^2$ directly as a function of pressure and temperature:

$$\frac{1}{c^2} = \frac{A + BP + CP^2 + DP^3}{E + FP} \tag{4}$$

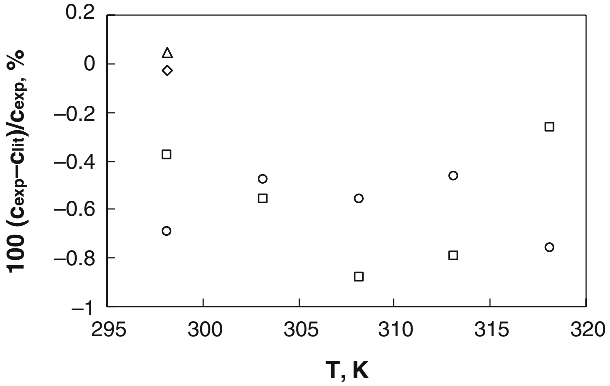

Fig. 3. Deviations (%) between the sound speed of DEGDME at atmospheric pressure, c_{exp} of this work and literature values c_{lit} at different temperatures: □ [24]; ○ [25]; △ [22]; ◇ [23].

in which

$$A = A_0 + A_1 T + A_2 T^2 + A_3 T^3 \tag{5}$$

and

$$E = 1 + E_1 T \tag{6}$$

Table II shows the values of the fitted coefficients for MEGDME and DEGDME.

Table II. Parameters of Eqs. (4)–(6) with c in $\mathrm{m \cdot s^{-1}}$, T in K, and P in MPa

	MEGDME	DEGDME
A_0	-7.75290×10^{-7}	-2.11330×10^{-7}
A_1	8.60714×10^{-9}	3.28646×10^{-9}
A_2	-2.42030×10^{-11}	-7.70310×10^{-12}
A_3	2.49154×10^{-14}	7.39181×10^{-15}
B	1.94766×10^{-9}	1.38248×10^{-9}
C	-7.34690×10^{-12}	-4.21070×10^{-12}
D	1.99793×10^{-14}	9.90601×10^{-15}
E_1	-1.98756×10^{-3}	-1.82032×10^{-3}
F	6.81114×10^{-3}	5.78442×10^{-3}
AD (%)	-5.9×10^{-3}	5.0×10^{-4}
AAD (%)	2.1×10^{-2}	1.8×10^{-2}
MD (%)	9.1×10^{-2}	7.0×10^{-2}

Subsequently, P-c-T relationships were used to evaluate the densities, isobaric thermal expansion coefficients, and both isentropic and isothermal compressibilities up to 100 MPa, by using a modification of the method suggested by Davis and Gordon [26] (inverse method). The density values at the reference pressure required to initiate this iterative procedure (in this case, at atmospheric pressure) were taken from literature data [10] and were expressed as a cubic function of temperature in the range investigated:

$$\rho\,(P_{\text{ref}}, T) = \rho_0 + \rho_1 T + \rho_2 T^2 + \rho_3 T^3 \tag{7}$$

Similarly, in order to obtain heat capacities at atmospheric pressure, literature values [27–32] were fitted to a second-order polynomial function:

$$C_P\,(P_{\text{ref}}, T) = C_{P_0} + C_{P_1} T + C_{P_2} T^2 \tag{8}$$

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

The densities and isothermal compressibility up to 100 MPa obtained with this procedure, which is the inverse method, are presented in Tables IV and V. The following Tait-like equation was fitted to the obtained density values:

$$\frac{1}{\rho\,(P, T)} - \frac{1}{\rho\,(P_{\text{ref}}, T)} = a \ln\left(\frac{P + b}{P_{\text{ref}} + b}\right) \tag{9}$$

where P_{ref} is again atmospheric pressure (0.1013 MPa), $\rho(P_{\text{ref}}, T)$ is defined by Eq. (7), and the a and b parameters are expressed as a func-

Table III. Parameters of Density, ρ in $\text{kg}\cdot\text{m}^{-3}$, and Heat Capacity, C_p in $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$, Correlation Functions (with T in K) at Atmospheric Pressure (Eqs. (7) and (8))

	MEGDME	DEGDME
ρ_0	1.57994×10^3	1.23930×10^3
ρ_1	-5.01166	-1.10477
ρ_2	1.30804×10^{-2}	5.84753×10^{-4}
ρ_3	-1.46160×10^{-5}	-8.79390×10^{-7}
Cp_0	2.95650×10^3	2.25468×10^3
Cp_1	-6.99657	-2.52962
Cp_2	1.40106×10^{-2}	6.37871×10^{-3}

Table IV. Densities (ρ) of Liquid Monoethylene Glycol Dimethyl Ether (MEGDME) and Diethylene Glycol Dimethyl Ether (DEGDME) at Temperature T and Pressure P

	T (K)						
	293.15	303.15	313.15	323.15	333.15	343.15	353.15
P (MPa)	ρ (kg $\cdot$ m^{-3})						
MEGDME							
0.1	866.65	855.55	844.41	833.14	821.65	809.85	797.67
10	875.35	864.93	854.51	844.03	833.40	822.56	811.44
20	883.37	873.50	863.66	853.81	843.85	833.75	823.43
30	890.77	881.35	872.00	862.65	853.24	843.72	834.03
40	897.65	888.62	879.68	870.75	861.79	852.74	843.57
50	904.11	895.41	886.81	878.24	869.66	861.02	852.28
60	910.19	901.79	893.49	885.23	876.98	868.68	860.30
70	915.95	907.81	899.77	891.79	883.82	875.82	867.77
80	921.42	913.52	905.72	897.99	890.27	882.53	874.75
90	926.65	918.95	911.37	903.85	896.36	888.86	881.32
100	931.65	924.14	916.75	909.44	902.15	894.85	887.54
DEGDME							
0.1	943.53	933.63	923.68	913.68	903.63	893.52	883.35
10	950.66	941.19	931.71	922.20	912.68	903.14	893.59
20	957.37	948.27	939.18	930.09	921.01	911.94	902.89
30	963.66	954.89	946.13	937.40	928.68	920.00	911.37
40	969.60	961.11	952.64	944.21	935.82	927.47	919.18
50	975.23	966.99	958.78	950.61	942.49	934.43	926.45
60	980.59	972.57	964.59	956.66	948.78	940.97	933.25
70	985.71	977.89	970.11	962.39	954.73	947.15	939.66
80	990.61	982.97	975.38	967.85	960.38	953.00	945.72
90	995.32	987.84	980.42	973.06	965.77	958.57	951.48
100	999.85	992.53	985.26	978.06	970.93	963.89	956.97

tion of temperature using second-order polynomial functions:

$$a = a_0 + a_1 T + a_2 T^2, \tag{10}$$

$$b = b_0 + b_1 T + b_2 T^2. \tag{11}$$

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 VI for both compounds. Examination of these deviations shows that this two-dimensional function (Eq. (9)) can match the density data within the experimental uncertainty ($0.1\,\mathrm{kg} \cdot \mathrm{cm}^{-3}$).

Table V. Isothermal Compressibility (κ_T) of Liquid Monoethylene Glycol Dimethyl Ether (MEGDME) and Diethylene Glycol Dimethyl Ether (DEGDME) at Temperature T and Pressure P

	T (K)						
	293.15	303.15	313.15	323.15	333.15	343.15	353.15
P (MPa)	κ_T (GPa^{-1})						
MEGDME							
0.1	1.0803	1.1731	1.2799	1.4038	1.5503	1.7194	1.9210
10	0.9572	1.0389	1.1275	1.2236	1.3312	1.4495	1.5831
20	0.8693	0.9378	1.0087	1.0855	1.1689	1.2602	1.3634
30	0.8003	0.8563	0.9159	0.9791	1.0471	1.1207	1.2016
40	0.7414	0.7897	0.8402	0.8937	0.9503	1.0110	1.0777
50	0.6919	0.7338	0.7781	0.8231	0.8715	0.9229	0.9790
60	0.6491	0.6862	0.7247	0.7631	0.8062	0.8503	0.8982
70	0.6123	0.6456	0.6788	0.7139	0.7508	0.7895	0.8312
80	0.5797	0.6095	0.6395	0.6706	0.7032	0.7373	0.7739
90	0.5509	0.5776	0.6048	0.6329	0.6621	0.6923	0.7248
100	0.5252	0.5493	0.5742	0.5996	0.6258	0.6530	0.6822
DEGDME							
0.1	0.7937	0.8524	0.9167	0.9873	1.0643	1.1493	1.2426
10	0.7302	0.7803	0.8338	0.8918	0.9541	1.0213	1.0942
20	0.6786	0.7210	0.7661	0.8147	0.8664	0.9220	0.9807
30	0.6340	0.6709	0.7103	0.7515	0.7956	0.8419	0.8910
40	0.5959	0.6285	0.6626	0.6987	0.7369	0.7765	0.8179
50	0.5628	0.5917	0.6219	0.6537	0.6869	0.7216	0.7578
60	0.5338	0.5595	0.5868	0.6148	0.6444	0.6749	0.7064
70	0.5077	0.5313	0.5556	0.5809	0.6074	0.6344	0.6625
80	0.4846	0.5060	0.5281	0.5510	0.5748	0.5992	0.6242
90	0.4638	0.4833	0.5035	0.5243	0.5460	0.5680	0.5905
100	0.4448	0.4628	0.4815	0.5005	0.5203	0.5403	0.5608

The densities ρ evaluated from the experimental P-c-T relationships (Table IV) were compared with those reported by Comuñas et al. [10], measured from 293.15 to 353.15 K and up to 60 MPa (Fig. 4 and Table VII). Average absolute deviations (AADs) of 0.022% and 0.026%, and maximum deviations (MDs) of 0.073% and 0.065% were observed for monoglyme and diglyme, respectively, in the overall literature P-T range. In Table VII, we also present the results corresponding to other two glymes (TrEGDME and TEGDME) for which densities under pressure and temperature have been reported previously by our group [15] and by Comuñas et al. [33]

Table VI. Parameters of the Tait Equation (Eqs. (9)–(11)) with ρ in $\mathrm{kg \cdot m^{-3}}$, κ_T in $\mathrm{GPa^{-1}}$, T in K, and P in MPa

	MEGDME	DEGDME
a_0	4.35690×10^{-5}	-4.16830×10^{-6}
a_1	-7.71810×10^{-7}	-4.72680×10^{-7}
a_2	9.39841×10^{-10}	5.76343×10^{-10}
b_0	3.38281×10^{2}	4.16982×10^{2}
b_1	-1.09762	-1.35073
b_2	7.74706×10^{-4}	1.05119×10^{-3}
AD (%) (ρ)	-7.3×10^{-4}	-4.8×10^{-4}
AAD (%) (ρ)	4.3×10^{-3}	2.5×10^{-3}
MD (%) (ρ)	1.5×10^{-2}	7.8×10^{-3}
AD (%) (κ_T)	2.2×10^{-1}	1.5×10^{-1}
AAD (%) (κ_T)	4.8×10^{-1}	3.5×10^{-1}
MD (%) (κ_T)	2.0	1.0

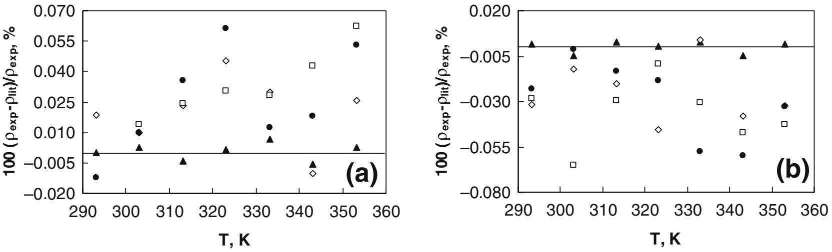

Fig. 4. Deviations (%) between the density ρ_{exp} deduced from acoustic measurements and those of Comuñas et al. [10] ρ_{lit} for several isobars: ▲, $P = 0.1$ MPa; ◇, $P = 20$ MPa; ●, $P = 40$ MPa; □, $P = 60$ MPa; (a) MEGDME, (b) DEGDME.

Table VII. Deviations between Different Thermophysical Properties Calculated from Literature *PVT* Data [10, 33] (Direct Method) and Those Determined from Experimental Acoustic Measurements [15, This Work] (Inverse Method)

	AAD (%)				MD (%)			
	ρ	κ_T	α_P	c	ρ	κ_T	α_P	c
MEGDME	2.2×10^{-2}	0.39	0.66	0.32	7.3×10^{-2}	0.84	3.09	0.84
DEGDME	2.6×10^{-2}	0.70	0.26	0.60	6.5×10^{-2}	1.53	0.69	1.01
TrEGDME	1.1×10^{-2}	0.11	0.29	0.15	2.6×10^{-2}	0.24	0.87	0.29
TEGDME	5.1×10^{-3}	0.10	0.24	0.10	2.4×10^{-2}	0.21	0.72	0.23

Also, we have compared the results of isothermal compressibilities, κ_T, as well as of isobaric thermal expansion coefficients, α_P, for the four glymes obtained in a previous paper [15] and in the present work from acoustic measurements, with those due to Comuñas et al. [10, 33]. For the case of κ_T comparisons were performed along isotherms spaced at 10 K increments from 293.15 to 353.15 K for pressures between 10 and 50 MPa at 10 MPa intervals, whereas for α_P they were performed between 303.15 and 343.15 K at 10 K steps and at pressures of 0.1 MPa and from 10 to 60 MPa at 10 MPa intervals. In Table VII, we present the obtained AAD (%) together with the MD (%). As can be seen in this table, our results agree with those of Comuñas et al. For α_P the poorest results are obtained for diglyme, an AAD of 0.66% (Fig. 5b) and a MD of 3.09%, with those reported by Comuñas et al. [10], whereas for κ_T the worst results are obtained for monoglyme, with an AAD of 0.70% and an MD of 1.53% (Fig. 5a). In addition, for all the properties the best results correspond to TEGDME.

Moreover, we have used the direct method to determine the speeds of sound from volumetric literature data for these last four glymes [10, 33], following the procedure proposed recently by Hartmann et al. [34]. For this purpose it is necessary to know not only the density as a function of pressure and temperature, but also the temperature dependence of the heat capacities along one reference isobar. Thus, the thermodynamic relation used in this procedure is

$$c^2 = \gamma \left(\frac{\partial P}{\partial \rho} \right)_T = \frac{C_P}{C_P - \left(T\alpha_{P2}/\rho\kappa_T \right)} \frac{1}{\rho\kappa_T} \tag{12}$$

where γ is the heat capacity ratio,

$$\gamma = C_P/C_V = \kappa_T/\kappa_S \tag{13}$$

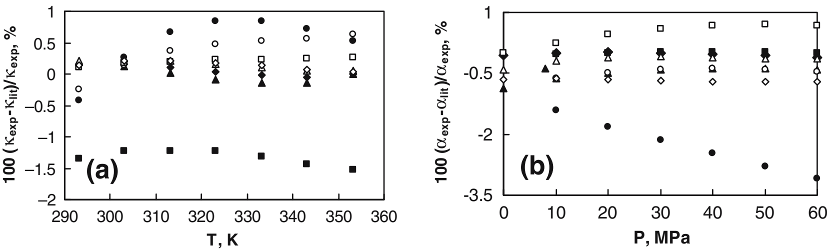

Fig. 5. Deviations (%) between the (a) κ_T and (b) α_P values deduced from acoustic measurements and those of Comuñas et al. [10, 33] for: (•, ○) monoglyme; (■, □) diglyme; (▲, △) triglyme; (♦, ◇) tetraglyme. Filled and unfilled symbols are the values at (a) 10 MPa and 50 MPa, and (b) 303.15 and 343.15 K, respectively.

For the temperature dependence of the densities and the heat capacities at 0.1 MPa of the four glymes, we have used Eqs. (7) and (8), together with the parameters given in Table III for the case of MEGDME and DEGDME. For TrEGDME and TEGDME, the parameters of Eqs. (7) and (8) were reported previously [15].

The heat capacities as a function of pressure and temperature can be evaluated taking into account that

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 (1/\rho)}{\partial T^2}\right)_P \tag{14}$$

Thus, the speeds of sound have been determined using Eqs. (12)–(14) from 303.15 to 343.15 K and from 10 to 50 MPa. Deviations between the speeds of sound derived from this procedure (calculated from literature *PVT* data, i.e., by the direct method) and the experimental results are also presented in Table VII for the four glymes. An example of the comparisons is presented in Fig. 6 for the four compounds. The comparison shows quite acceptable results, although in the case of MEGDME and DEGDME the AADs are larger than the sound-speed experimental uncertainty (0.2%), whereas for TrEGDME and TEGDME the deviations are lower than this uncertainty.

Analyzing the behavior of the last properties with the chain length of the glyme, it is observed that speeds of sound and densities increase with an increase in the chain length of the glyme, contrary to the behavior of isobaric thermal expansion coefficients and to both isentropic and isothermal compressibilities. This behavior is mainly due to the stronger dipole–dipole interaction in the higher members of the series, caused by the introduction of new polar ether groups in the molecular structure.

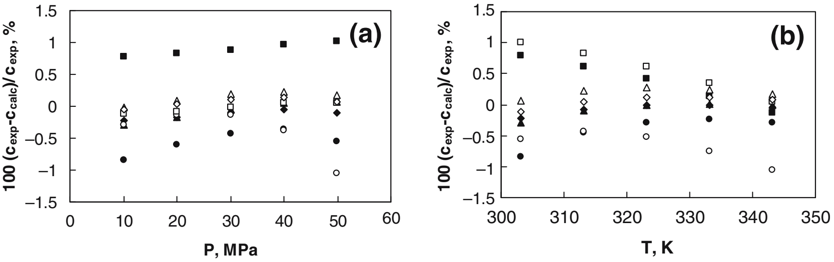

Fig. 6. Deviations (%) between the experimental speed of sound, c_{exp}, and those deduced from volumetric data of Comuñas et al. [10, 33], c_{lit}, for: (•, ○) monoglyme; (■, □) diglyme; (▲, □) triglyme; (♦, ◇) tetraglyme. Filled and unfilled symbols are the values at (a) 303.15 and 343.15 K, and (b) 10 MPa and 50 MPa, respectively.

Thus, the increase of density with chain length involves a major compactness of the molecule and consequently a lower free intermolecular space. Hence, the capacity of the liquid to expand or contract will also decrease [35], as observed, because α_P and κ_T diminish when the glyme chain length increases. Considering this fact, Douheret et al. [2] indicate that the evaluation of derived properties, with κ_T the most important, provide a valuable aid in the characterization of intermolecular forces, pointing out that the more accurate and precise method to calculate κ_T is from a knowledge of κ_S, and thus from ultrasonic speeds. In addition, the isentropic compressibility provides more information on the intensity of intermolecular interactions in liquids [36]. A larger intensity of intermolecular interactions corresponds to a lower isentropic compressibility, which is consistent again with the obtained results.

Moreover, in order to propagate the sound, successive layers must be put into motion, and the transmission of the perturbation from one layer to the next will be facilitated in liquids with strong bonds between molecules [37]. Accordingly, the sound speed increases when the chain length of the glyme increases, that is, the number of polar ether groups grows.

We have also performed a comparison of the results obtained for glymes with those of the corresponding alkanes, i.e., hexane, nonane, dodecane, and pentadecane with MEGDME, DEGDME, TrEGDME, and TEGDME, respectively; the molar masses of the alkanes are slightly less than the corresponding glyme values, especially for the lower members of the series. So, the density of glymes is appreciably higher than that of alkanes [38]; this fact shows the lower molar volume of glymes and consequently the best packing of molecules, which is in concordance with the strong interactions present in glymes. Thus, glymes have lower thermal expansion coefficients and compressibilities than alkanes [21, 39–41]. Furthermore, glymes have appreciably higher viscosities [33, 42, 43], boiling points (and thus lower vapor pressures [44, 45]), and slightly higher speed-of-sound values than alkanes [21, 39–41].

On the other hand, in real applications lubricating oils could be contaminated with water or other substances due to ambient moisture and malfunctioning of devices. Small quantities of water, on the order of 1% in volume, can alter the lubricating characteristics of the oil. Then it is necessary to have a continuous analysis of the oil. In this sense, a liquid can be characterized by its physical properties, such as density, viscosity, thermal conductivity, or dielectric permittivity. Another possibility is to measure acoustic parameters such as the propagation velocity, attenuation coefficient, and acoustic impedance, using ultrasound. These parameters can be used to nondestructively evaluate variables of industrial processes, such as the concentration of particles in emulsions and suspensions [46] and lubricant film measurements.

The acoustic impedance (Z) of a medium is a property causing resistance to the propagation of ultrasound. The acoustic impedance is defined as the product of density (ρ) and acoustic velocity (c) of that medium ($Z=\rho c$). We have determined this property only from acoustic measurements. As expected, the acoustic impedance shows the same trend as the density and the speed of sound; it increases with the chain length of the glyme and with the pressure, whereas it decreases with an increase in the temperature, as can be seen in Fig. 7.

In addition, we have determined the acoustic nonlinearity parameter, B/A, which can be expressed as

$$\frac{B}{A}=2\rho c\left(\frac{\partial c}{\partial P}\right)_S=2\rho c\left(\frac{\partial c}{\partial P}\right)_T+\frac{2cT\alpha_P}{C_P}\left(\frac{\partial c}{\partial T}\right)_P=\left(\frac{B}{A}\right)'+\left(\frac{B}{A}\right)'' \qquad (15)$$

This parameter plays a significant role in characterizing the nonlinear acoustic phenomena associated with the medium, and, hence, its determination is of increasing interest in a number of areas. This parameter is important for two reasons: it is a basic parameter of a fluid, which can be related to the molecular dynamics of the medium, and it determines the distortion of a finite amplitude wave traveling through the fluid [47]. Indeed, it is a measure of the variation of the medium caused by the sound field [48], and can be used as a complementary parameter in the characterization of liquids [49].

When the speed of sound is well known in a broad P-T range, as in the present case, B/A can be estimated by, namely, the thermodynamic method by applying the right term of Eq. (15). The uncertainty of the B/A values determined by using this method are about 5% [50, 51].

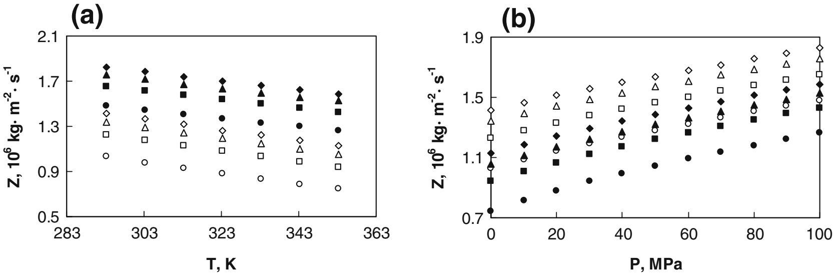

Fig. 7. Acoustic impedance, Z, of ○, monoglyme; □, diglyme; △, triglyme; ◇, tetraglyme. Filled and open symbols are, respectively, the values at (a) 0.1 and 100 MPa and (b) 293.15 and 353.15 K.

This parameter was determined using the experimental and estimated speeds of sound; both sets of B/A values, up to 60 MPa, give an AAD ranging from 4% for tetraglyme up to 10% for monoglyme. The B/A values determined from experimental speeds of sound were found to increase with the chain length of the glyme and with the inverse of the sound velocity, and to decrease with density along isotherms. We must point out that B/A, determined with the speeds of sound estimated from volumetric data, does not show a regular trend with the chain length of the glyme. The strong differences between both sets of B/A values are attributable to the accumulation of uncertainties corresponding to the successive derivatives of the direct method.

In Fig. 8, we can observe that the dependence of B/A on pressure is stronger than on temperature, showing a decreasing trend in the case of pressure and being, up to a reasonable extent, temperature-independent. The values of $(B/A)''$ are negative for the four liquids and their absolute values are far less than those of $(B/A)'$. Thus, the value of B/A is mainly dependent on the value of $(B/A)'$, which expresses the increase in phase velocity brought about by pressure, whereas $(B/A)''$ gives the increase due to temperature [52].

As usual, also in the estimation process of the nonlinearity parameter, the pressure derivatives are calculated more accurately than the temperature derivatives. The contribution to the (B/A) uncertainty due to the temperature derivatives, affect only the $(B/A)''$ values. Hence, the (B/A) uncertainty is dominated by the uncertainty of $(B/A)'$, which is affected mainly by the goodness of $(\partial c/\partial P)_T$.

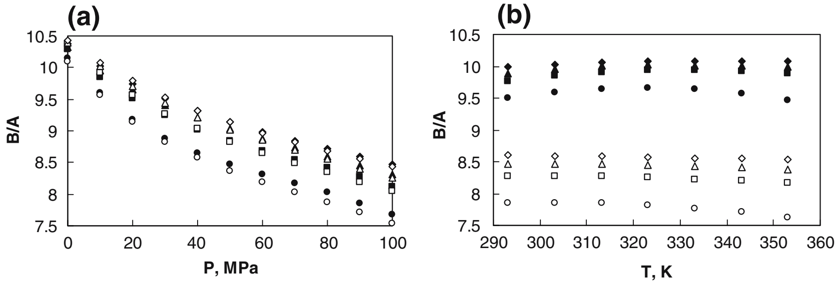

Fig. 8. Nonlinearity parameter B/A of (○, •) monoglyme; (□, ■) diglyme; (▲, △) triglyme; (♦, ◇) tetraglyme, (a) versus pressure at 303.15 K (filled symbols) and 343.15 K (open symbols), and (b) versus temperature at 10 MPa (filled symbols) and 90 MPa (open symbols).

4. CONCLUSIONS

In this work, several thermophysical properties of monoethylene glycol dimethyl ether (MEGDME) and diethylene glycol dimethyl ether (DEGDME), that is, speeds of sound, the *PVT* surface, and isothermal and isentropic compressibilities, have been determined from direct acoustic measurements at temperatures from 283.15 to 353.15 K and at pressures to 100 MPa. In the case of densities and isothermal compressibilities, comparisons between the reported values and literature data determined by densimetry up to 60 MPa reveal excellent consistency, concluding that the differences are close to the uncertainties of both experimental methods. A similar analysis has been performed previously for TrEGDME and TEGDME. Thus, we have analyzed the behavior of the properties as a function of the chain length of the glymes from MEGDME to TEGDME. Speeds of sound and densities increase with an increase in the chain length of the glyme, whereas the thermal expansion coefficients and both isentropic and isothermal compressibilities decrease.

In addition, we have compared the results for the glymes with those of corresponding alkanes with similar molar masses. The comparison was extended to other properties available in the literature such as the viscosity or boiling points, which give larger values for glymes than for the corresponding alkanes. This analysis shows the importance of the strong dipole–dipole interactions present in glymes, especially in higher members of the series, caused by the introduction of new ether groups (which are polar) in the molecular structure.

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