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$p\rho T$ Measurements of Polyethylene Glycol Dimethylethers Between 278.15 and 328.15 K at Pressures to 12 MPa

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In this paper we present a new experimental apparatus designed to measure pressure–density–temperature ($p\rho T$) properties with a high-pressure vibrating tube densimeter. Data reliability has been verified by comparing our experimental results for methanol, *n*-heptane, toluene, and HFC-134a with literature data. In this work we also report new experimental densities from 278.15 to 328.15 K, and up to 12 MPa, of triethylene glycol dimethylether (TrEGDME) and tetraethylene glycol dimethylether (TEGDME). The isobaric thermal expansion coefficients, isothermal compressibility, and internal pressure have been calculated. The dependence of these properties on the length of polyethylene glycol dimethylether, $CH_3O\text{–}((CH_2)_2O)_n\text{–}CH_3$, is analyzed.

KEY WORDS: density; high pressure; internal pressure; isobaric thermal expansion coefficients; isothermal compressibilities; liquid; polyethylene glycol dimethylethers.

1. INTRODUCTION

This work continues the research [1–3] on thermophysical properties of new working fluids for heat pump systems. In this work we have chosen the polyethylene glycol dimethylethers, $CH_3O\text{–}((CH_2)_2O)_n\text{–}CH_3$ due to their application as absorbents in absorption engines and as lubricants for the HFCs in refrigeration compressors [4–7].

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Polyalkylene glycol dimethylethers are good candidates as absorbents for several refrigerants because they have good thermal and chemical stability, and their boiling temperatures are higher than for several of the refrigerants proposed [4–6] for absorption cycles, such as methanol, TFE, HFCs, etc. In addition, polyalkylene glycol dimethylethers present a strong affinity to small polar molecules, which results in their high solubility in these refrigerants. In order to determine the cycle performance, it is necessary to know various properties and, in particular, the density of both the pure liquids and their mixtures as functions of pressure, temperature, and composition.

Mineral oils, which were formerly used as lubricants with the CFCs, do not fulfill the requirements of the lubricants suitable for refrigeration compressors operating with the HFCs. For this purpose, the automotive industry has selected polyalkylene glycol-based lubricants (PAGs) for their climate control systems using HFC-134a [7, 8]. Furthermore, PAGs are soluble in ammonia, which is widely used in refrigeration systems [9]. Density data are among those thermophysical properties whose knowledge is required to determine the reliability of polyalkylene glycols for use as lubricants in refrigeration compressors [10].

In the literature, we have found measurements for tetraethylene glycol dimethylether ($n=4$) by Svejda et al. [11] at 293.15 K and up to 10 MPa. In the case of diethylene glycol dimethylether ($n=2$), Senger [12] has reported some measurements (from 298.15 to 328.15 K and up to 202 MPa). For ethylene glycol dimethylether ($n=1$), there are density data by Senger [12] for the same ranges of temperature and pressure and by Sharipov and Bairamova [13] from 288.0 to 473.0 K and up to 37 MPa. Furthermore, Conesa et al. [14] have determined the densities of $CH_3O{-}(CH_2)_2O)_n{-}CH_3$ for $n=1$ to 5 at 1 MPa and from 283.15 to 423.15 K. Recently, the densities of PEGDME 300 up to 30 MPa and from 298 to 338 K have been published by Lee et al. [15].

In this work we present experimental densities of the triethylene glycol dimethylether (TrEGDME) and tetraethylene glycol dimethylether (TEGDME) in the pressure range from 0.1 to 12 MPa and from 278.15 to 328.15 K. The measurements were performed with a vibrating tube densimeter.

2. EXPERIMENTAL

2.1. Materials

Toluene and 2,2,4-trimethylpentane (Aldrich; mole fraction, >0.998), methanol (Aldrich; mole fraction, >0.999), dichloromethane (Aldrich;

mole fraction, >0.996), TrEGDME and TEGDME (Aldrich; mole fraction, >0.99), *n*-heptane (Fluka; mole fraction, >0.995), and HFC-134a (Solvay Fluor and Derivate; >0.995) were subjected to no further purification other than drying with Union Carbide 0.4-nm molecular sieves. Chemical liquid purities were checked by gas chromatography, and they were found to be 2,2,4 trimethylpentane (99.92), dichloromethane (99.99), *n*-heptane (99.8), toluene (99.99), methanol (99.99), HFC-134a (99.5), TrEGDME (99.7), and TEGDME (99.9).

2.2. Experimental Apparatus

We have used an Anton Paar DMA 60/512P vibrating tube densimeter to determine the density as a function of pressure and temperature. This type of densimeter is adequate to perform measurements in a broad range of temperature (from 263.15 to 423.15 K) and pressure (from 0 to 70 MPa) but requires the construction and setup of several pieces of equipment and peripherals. Several authors have already published different flow diagrams of their equipment [16–19]. In our case the apparatus was designed as indicated in Fig. 1.

The control of the temperature of the vibrating tube cell is performed through a thermostatic bath Polyscience PS 9110, which regulates the temperature to within a precision of better than ±0.003 K. The temperature is measured inside the cell block with an Anton Paar CKT100 platinum resistance thermometer with a resolution of 0.001 K, which, however, was

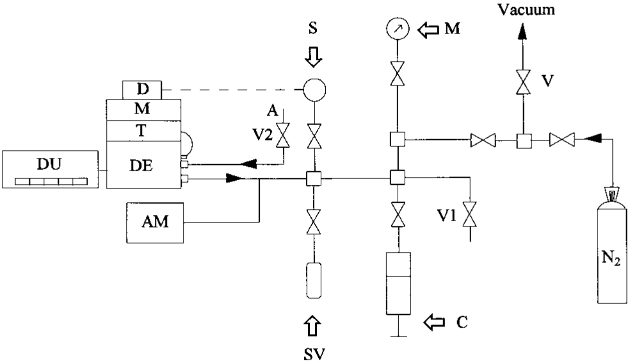

Fig. 1. Flow diagram of the apparatus: V, valves; SV, security valve; S, pressure transducer (Setra C204); D, pressure indicator (DATUM 2000); M, multimeter (Keithley 2000); T, thermometer (Anton Paar CKT100); DE, densimeter (Anton Paar 512P); DU, frequency meter (Paar DMA60); AM, absolute manometer (Ruska 6230); M, manometer; C, compressor (HiP Model 50-6-15).

calibrated to an uncertainty of 0.01 K. The densimeter measuring unit used in this work reports the vibration period to seven significant digits.

The pressure of the system was applied with a piston pressure intensifier (HiP Model 50-6-15) and measured on an absolute manometer Ruska 6230. The resolution of this manometer is better than 0.0001MPa, although its calibration has an uncertainty of 0.001 MPa and the fluctuations of the pressure are ±0.002 MPa.

Before loading each sample, the densimeter and all tubing were washed with a volatile liquid, such as acetone, to ensure removal of any residue from previous runs. Then, gaseous nitrogen was passed through all the system. Once this cleaning process was completed, vacuum was applied to the system for several hours. Then, valve V2 was opened, introducing the sample through tube A. When thermal equilibrium was reached, the vibration period of the cell was determined at different pressures, starting at 12 MPa, followed by the lower pressures. Then the temperature of the liquid bath was changed and a new isotherm started.

2.3. Experimental Method

One of the most important problems in using vibrating tube densimeters is to relate the raw data (period of vibration τ) to the density ρ, i.e., the calibration curve expressed as the apparatus constants. The density ρ is related to the vibration period τ by the equation,

$$\rho(T, p) = A(T, p)\, \tau^2(T, p) - B(T, p) \tag{1}$$

where $\rho(T, p)$ is the density of the fluid contained in the densimeter, and $A(T, p)$ and $B(T, p)$ are characteristic parameters which must be determined by calibration with two fluids of well-known densities (ρ_1 and ρ_2, respectively) over broad ranges of temperature and pressure. These characteristic parameters are given by

$$\begin{aligned} A(T, p) &= \frac{\rho_1(T, p) - \rho_2(T, p)}{\tau_1^2(T, p) - \tau_2^2(T, p)} \\ B(T, p) &= \rho_1(T, p) + A(T, p)\, \tau_1^2(T, p) \end{aligned} \tag{2}$$

where τ_1 and τ_2 are the vibration periods of fluids 1 and 2.

The calibration parameters, A and B, were determined with different calibrating fluid pairs, with the aim of verifying whether $A(T, p)/B(T, p)$ is independent of the pressure as Lagourette et al. [18] have found, as well as to analyze the pressure and the temperature dependences of $A(T, p)$. In

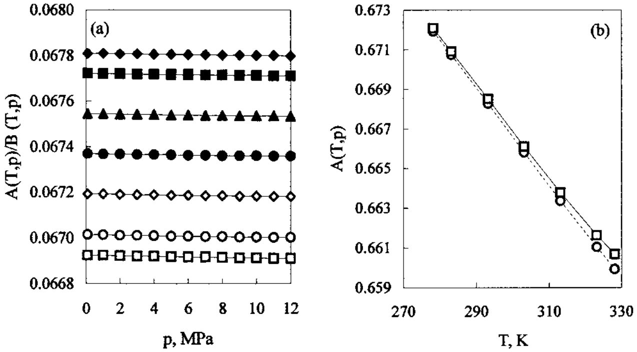

Fig. 2. (a) Ratio of the characteristic parameters of the vibrating tube, $A(T, p)/B(T, p)$, versus pressure: (◆) 278.15 K; (■) 283.15 K; (▲) 293.15 K; (●) 303.15 K; (◇) 313.15 K; (○) 323.15 K; (□) 328.15 K. (b) Characteristic parameter, $A(T, p)$, versus temperature for two pressures: (□) 0.1 MPa; (○) 12 MPa.

Fig. 2 we show both the $A(T, p)/B(T, p)$ ratio and $A(T, p)$ obtained using 2,2,4-trimethylpentane and dichloromethane. These quantities show strong variation with temperature and are slightly dependent on pressure. The small pressure influence on $A(T, p)$ is also in agreement with the results obtained by Galicia-Luna et al. [19]. We have verified that this behavior remains the same for the following calibration pairs: 2,2,4-trimethylpentane–dichloromethane, nitrogen–dichloromethane, toluene–dichloromethane, 2,2,4-trimethylpentane–toluene, and nitrogen–toluene.

When using a vibrating tube densimeter, it is convenient to use calibrating fluids with densities both higher and lower than the sample to be analyzed. For that reason, and in order to measure the density of polyethylene glycol dimethylethers, we have chosen as calibrating fluids, 2,2,4-trimethylpentane and dichloromethane.

The densities of 2,2,4-trimethylpentane have been calculated from the Pádua et al. [20] experimental data correlation, which represents their values with a standard deviation better than 0.03%. In the case of dichloromethane, we have used the experimental values of Demiriz [21] and the densities published in the TRC [22]. We have correlated all these data to an equation of the Tait type. This equation represents the data with a standard deviation of 0.03%.

The experimental precision of the density, estimated by taking into account the inaccuracies of temperature, pressure, period, and density of the reference fluids, is 20×10^{-5} $g \cdot cm^{-3}$. The main contribution to the density uncertainty is the precision of the experimental densities of the calibrating fluids. In order to improve the accuracy, more precise density

Table I. Experimental Densities ρ ($g \cdot cm^{-3}$) of Pure Compounds at Different Temperatures T and Pressures p

	T (K)				
p (MPa)	283.15	293.15	303.15	313.15	323.15
n-Heptane					
0.48	0.69231	0.68417	0.67560	0.66719	0.65861
0.96	0.69271	0.68461	0.67608	0.66771	0.65916
2.04	0.69361	0.68560	0.67715	0.66886	0.66039
3.01	0.69440	0.68647	0.67808	0.66987	0.66148
3.97	0.69518	0.68732	0.67900	0.67086	0.66253
5.07	0.69607	0.68830	0.68004	0.67198	0.66372
6.03	0.69685	0.68914	0.68095	0.67295	0.66475
7.05	0.69767	0.69003	0.68191	0.67396	0.66583
8.08	0.69848	0.69090	0.68286	0.67496	0.66689
9.11	0.69926	0.69173	0.68377	0.67594	0.66795
10.14	0.70002	0.69254	0.68466	0.67691	0.66898
11.16	0.70076	0.69333	0.68553	0.67788	0.67000
12.19	0.70150	0.69413	0.68640	0.67885	0.67100
Toluene					
0.48	0.87658	0.86735	0.85799	0.84863	0.83925
0.96	0.87692	0.86770	0.85838	0.84904	0.83968
2.04	0.87766	0.86849	0.85923	0.84993	0.84065
3.01	0.87832	0.86919	0.85998	0.85075	0.84152
3.97	0.87896	0.86989	0.86072	0.85155	0.84237
5.07	0.87970	0.87070	0.86157	0.85246	0.84334
6.03	0.88037	0.87139	0.86232	0.85325	0.84418
7.05	0.88107	0.87214	0.86311	0.85409	0.84508
8.08	0.88177	0.87287	0.86390	0.85493	0.84598
9.11	0.88246	0.87357	0.86466	0.85574	0.84687
10.14	0.88313	0.87426	0.86543	0.85656	0.84775
11.16	0.88380	0.87494	0.86618	0.85739	0.84859
12.19	0.88448	0.87567	0.86694	0.85824	0.84948
Methanol					
0.48	0.80135	0.79210	0.78262	0.77316	0.76356
0.96	0.80175	0.79257	0.78309	0.77366	0.76408
2.04	0.80267	0.79355	0.78414	0.77479	0.76528
3.01	0.80350	0.79442	0.78506	0.77579	0.76633
3.97	0.80431	0.79529	0.78598	0.77677	0.76738
5.07	0.80525	0.79630	0.78702	0.77788	0.76854
6.03	0.80607	0.79714	0.78794	0.77886	0.76958
7.05	0.80693	0.79806	0.78892	0.77987	0.77066
8.08	0.80780	0.79896	0.78988	0.78088	0.77173
9.11	0.80863	0.79983	0.79082	0.78188	0.77279
10.14	0.80947	0.80070	0.79174	0.78287	0.77385
11.16	0.81028	0.80155	0.79265	0.78385	0.77488
12.19	0.81113	0.80243	0.79358	0.78486	0.77592

Table I. *(Continued)*

	T (K)				
p (MPa)	283.15	293.15	303.15	313.15	323.15
HFC-134a					
1		1.22814	1.18946		
2		1.23313	1.19554		1.10918
3		1.23790	1.20131		1.11888
4	1.27688	1.24367	1.20686	1.17031	1.12790
5	1.28088	1.24838	1.21217	1.17607	1.13609
6	1.28480	1.25291	1.21723	1.18246	1.14354
7	1.28862	1.25732	1.22280	1.18855	1.15077
8	1.29218	1.26158	1.22778	1.19436	1.15778
9	1.29583	1.26578	1.23257	1.19996	1.16436
10	1.29943	1.26985	1.23726	1.20539	1.17069
11	1.30293	1.27376	1.24180	1.21062	1.17698
12	1.30641	1.27766	1.24628	1.21572	1.18281

data are needed for the fluids used as references as stated by Compostizo et al. [23].

As explained below, to verify the experimental method, we have measured the densities of *n*-heptane, methanol, toluene, and HFC-134a over the same temperature and pressures ranges as those of the polyether compounds (from 283.15 to 323.15 K and up to 12 MPa). These experimental values are reported in Table I.

2.4. Analysis of the Experimental Method

With the aim of comparing the literature data with our experimental results obtained for different liquids, we have used different references among which we want to point out three articles by Cibulka et al. [24–26], where they present correlations obtained from one wide database (T, p, ρ) for several pure liquids.

The correlation method used by Cibulka et al. utilizes the following Tait equation:

$$\rho(T, p, \bar{c}, \bar{b}) = \frac{\rho(T, p_{\mathrm{ref}}(T))}{1 - C(T, \bar{c}) \ln[(B(T, \bar{b}) + p)/(B(T, \bar{b}) + p_{\mathrm{ref}}(T))]} \tag{4}$$

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

$$\rho(T, p_{\mathrm{ref}}(T)) = \sum_{i=0}^{N_A} A_i (T/100)^i \tag{5}$$

The denominator of Eq. (4) changes with both temperature and pressure. $C(T, \bar{c})$ and $B(T, \bar{b})$ have also been expressed using polynomial functions,

$$C(T, \bar{c}) = \sum_{i=0}^{N_C} c_i[(T - T_0)/100]^i \tag{6}$$

$$B(T, \bar{b}) = \sum_{i=0}^{N_B} b_i[(T - T_0)/100]^i \tag{7}$$

We have found the following results for heptane, methanol, toluene, and HFC-134a.

Heptane. In this case we have calculated the parameters of Eq. (5) by using densities at atmospheric pressure and temperatures in the range from 273.15 to 333.15 K available from TRC [22]. The parameters of Eqs. (6) and (7) were taken from Cibulka and Hnědkovský [24]. Our experimental results present deviations lower than 0.08% from the data calculated from this Tait equation, as can be seen in Fig. 3. In 1994, Assael et al. [27] have presented a new correlation, which covers the densities of alkanes (from methane to *n*-hexadecane). The deviations of our measurements for density from those calculated by their correlation are less than 0.10%. In Fig. 3 we have also plotted these deviations together with the differences between our experimental data and those of Malhotra and Woolf [28], which are always lower by 0.09%.

Toluene. For the comparison we have used the Tait equations due to Kashiwagi et al. [29] and to Sousa [30]. The deviations between our experimental results and those of both references are less than 0.06% (Fig. 3). Our data differ from the Malhotra and Woolf [31] correlated values by no more than 0.05%, but we must point out that the Tait equation used by these authors was determined from data at temperatures equal to or higher than 298.15 K. Thus, we have done an extrapolation for the lower temperatures. A very recent review by Cibulka and Takagi [25] was also utilized to check our results. The deviations between both sets are 0.04%.

Methanol. Similarly to what is done for heptane, the reference pressure of the Tait equation has been the atmospheric value, and the densities used to calculate the parameters of the numerator of Eq. (4) were taken from TRC data [22] in the temperature range from 273.15 to 333.15 K. The parameters of Eq. (6) were determined by Cibulka and Zirková [26]. The deviations between our experimental results and those obtained from this correlation were less than 0.06%, as can be seen in Fig. 4. We have

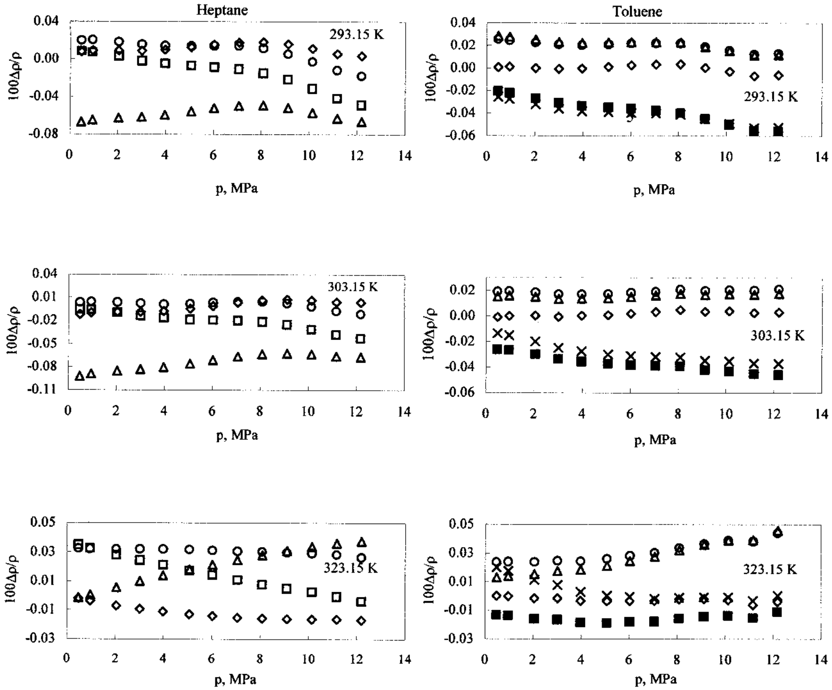

Fig. 3. Comparison between the experimental and the literature *pρT* data for heptane and toluene at different temperatures: (○) Cibulka and Hnědkovský [24]; Cibulka and Takagi [25]; (△) Malhotra and Woolf [28, 31]; (◇) Tait correlation; (□) Assael et al. [27]; (■) Kashiwagi et al. [29]; (×) Sousa [30].

also compared our results with those obtained by Hruby et al. [32], which showed deviations of less than 0.06% for all temperatures and pressures.

HFC-134a. We have performed experimental measurements of the density of HFC-134a from 283.15 to 323.15 K at pressures up to 12 MPa. Our experimental data differ from those of Tillner and Baehr [33] by less than 0.10% and from those of Morrison and Ward [34] by less than 0.09%, as can be seen in Fig. 4.

For comparison, in Figs. 3 and 4 we have also plotted the percentage residuals of the fits of our experimental values using a Tait equation. The differences between the densities calculated from the calibration curve and the corresponding references are consistent with the deviations obtained from the correlations of both calibration substances. More precise equations of state for the fluids used as references will improve the accuracy of our measurements.

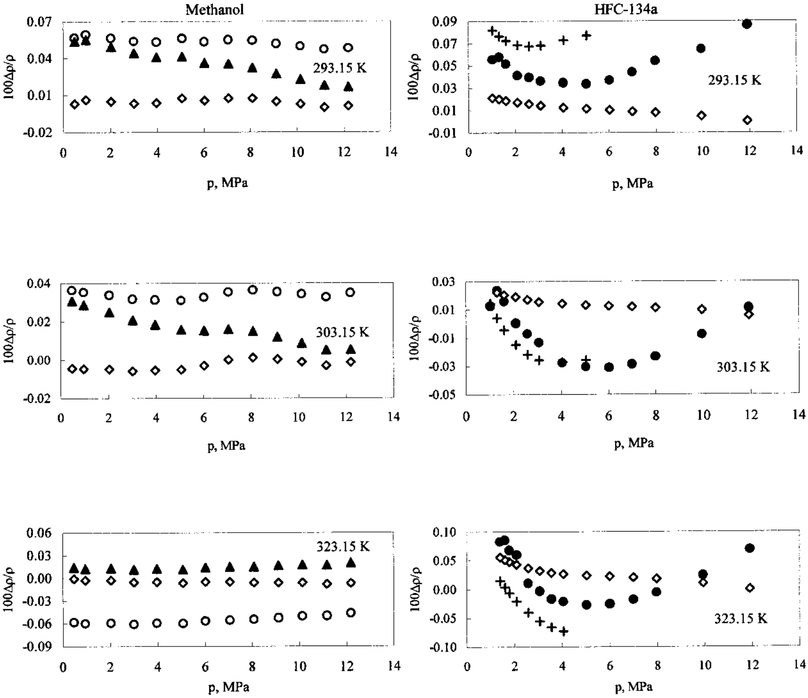

Fig. 4. Comparison between the experimental and the literature $p\rho T$ data for methanol and HFC-134a at different temperatures: (○) Cibulka and Zirková [26]; (◇) Tait correlation; (▲) Hruby et al. [32]; (●) Tillner and Baehr [33]; (+) Morrison and Ward [34].

3. RESULTS

The densities of TrEGDME and TEGDME have been measured along isotherms between 278.15 and 328.15 K at pressures to 12 MPa. In Table II, we present the experimental and literature densities at atmospheric pressure. For the higher pressures the experimental $p\rho T$ data are reported in Table III.

Following the method of Cibulka et al. [24–26], the (T, p, ρ) relation for the compressed liquid surface was represented for both ethers by the following modified Tait equation:

$$\rho(T, p) = \frac{\rho(T, p_{\mathrm{ref}}(T))}{1 - C \ln[(B(T) + p)/(B(T) + p_{\mathrm{ref}})]} \tag{8}$$

Table II. Densities, ρ, and Isobaric Thermal Expansion Coefficients, α_p, for the Pure Liquids at Atmospheric Pressure and Temperature T

	T (K)				
Component	283.15	293.15	303.15	313.15	323.15
		ρ $(\mathrm{g \cdot cm^{-3}})$			
TrEGDME	0.99464,^{a} 0.99499^b	0.98506,^{a} 0.98550^b	0.97544,^{a} 0.97594^b	0.96583,^{a} 0.96640^b	0.95625,^{a} 0.95699^b
TEGDME	1.01957,^{b} 1.02025^a 1.02048^c	1.01081,^{a} 1.01030^b 1.01101,^{c} 1.01093,^{d} 1.01126^d	1.00150,^{a} 1.00103^b 1.00185^c	0.99229,^{a} 0.99181^b 0.99270,^{c} 0.99274^d	0.98314,^{a} 0.98269^b 0.98323^c
		α $(\mathrm{K^{-1}})$			
TrEGDME	9.60,^{a} 9.45^b	9.76,^{a} 9.69^b	9.89,^{a} 9.80^b	9.98^a	10.04^a
TEGDME	9.35,^{a} 9.06^b	9.28,^{a} 9.18,^{b} 9.16^c	9.26,^{a} 9.24,^{b} 9.08^c	9.28,^{a} 9.33^c	9.35^a

[a] This work.

[b] Tovar et al. [37].

[c] Esteve et al. [38].

[d] Svejda et al. [11].

Table III. Experimental Densities ρ ($\mathrm{g \cdot cm^{-3}}$) of Pure Liquids at Different Temperatures T and Pressures p

	T (K)						
p (MPa)	278.15	283.15	293.15	303.15	313.15	323.15	328.15
				TrEGDME			
1	0.99993	0.99518	0.98563	0.97604	0.96644	0.95686	0.95210
2	1.00053	0.99581	0.98630	0.97675	0.96720	0.95767	0.95293
3	1.00113	0.99643	0.98696	0.97746	0.96795	0.95848	0.95376
4	1.00173	0.99705	0.98762	0.97816	0.96870	0.95927	0.95458
5	1.00233	0.99766	0.98828	0.97886	0.96945	0.96006	0.95539
6	1.00292	0.99827	0.98893	0.97955	0.97018	0.96085	0.95620
7	1.00351	0.99888	0.98958	0.98024	0.97092	0.96163	0.95701
8	1.00409	0.99948	0.99022	0.98093	0.97165	0.96240	0.95780
9	1.00467	1.00008	0.99086	0.98161	0.97237	0.96317	0.95859
10	1.00525	1.00068	0.99149	0.98229	0.97309	0.96393	0.95938
11	1.00583	1.00127	0.99213	0.98296	0.97380	0.96469	0.96016
12	1.00640	1.00186	0.99276	0.98363	0.97451	0.96544	0.96093
				TEGDME			
1	1.02554	1.02077	1.01135	1.00206	0.99286	0.98369	0.97912
2	1.02611	1.02136	1.01198	1.00273	0.99357	0.98445	0.97989
3	1.02668	1.02194	1.01260	1.00339	0.99427	0.98519	0.98065
4	1.02724	1.02252	1.01322	1.00405	0.99498	0.98594	0.98141
5	1.02780	1.02310	1.01384	1.00471	0.99567	0.98667	0.98217
6	1.02836	1.02368	1.01445	1.00537	0.99637	0.98740	0.98292
7	1.02892	1.02425	1.01507	1.00602	0.99706	0.98813	0.98367
8	1.02947	1.02483	1.01567	1.00666	0.99774	0.98886	0.98441
9	1.03002	1.02539	1.01628	1.00731	0.99842	0.98957	0.98514
10	1.03057	1.02596	1.01688	1.00795	0.99910	0.99029	0.98588
11	1.03111	1.02652	1.01748	1.00858	0.99977	0.99100	0.98660
12	1.03165	1.02708	1.01808	1.00921	1.00044	0.99170	0.98732

where $\rho(T, p_{\mathrm{ref}}(T))$, the temperature dependence of the density at the reference pressure of 0.1 MPa, is given by

$$\rho(T, p_{\mathrm{ref}}(T)) = A_0 + A_1 T + A_2 T^2 + A_3 T^3 \tag{9}$$

The values of the coefficients at 0.1 MPa have been determined from our experimental results in Table II.

In Eq. (8), the parameter C was assumed to be temperature independent, and for $B(T)$, we have used the following polynomial:

$$B(T) = B_0 + B_1 T + B_2 T^2 \tag{10}$$

Table IV. Parameters A_i, B_i, and C and Standard Deviation, σ, for Eq. (8)

Parameters	TrEGDME	TEGDME
A_0	1.0987439	1.530492
A_1	6.917547×10^{-4}	-3.249536×10^{-3}
A_2	-5.408636×10^{-6}	7.228162×10^{-6}
A_3	5.886742×10^{-9}	-7.473583×10^{-9}
C	0.091965	0.092420
B_0	785.7634	959.4443
B_1	-3.4146	-4.4400
B_2	4.072×10^{-3}	5.6972×10^{-3}
σ	10^{-5}	10^{-5}

The values of B_i and C were determined by fitting our experimental data with Eq. (7) at pressures different than 0.1 MPa with a Marquardt–Levenberg-type algorithm. For both polyethers the standard deviation from the Tait correlation of our experimental data is 10^{-5} g · cm^{-3}. The obtained values of A_i, B_i, and C are listed in Table IV.

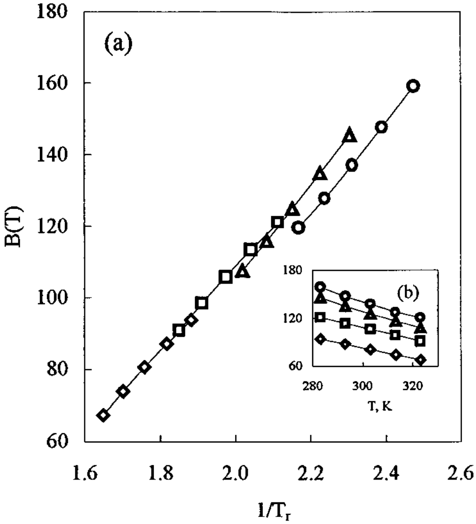

Fig. 5. Dependence of the parameter $B(T)$ of the Tait equation on (a) the reduced temperature T_r and (b) the temperature T for CH_3O–$((CH_2)_2O)_n$–CH_3. (◇) $n=1$; (□) $n=2$; (△) $n=3$; (○) $n=4$.

The function $B(T)$ is plotted in Fig. 5, where it is shown that $B(T)$ decreases with temperature and increases with the chain length of the polyether. This is in agreement with the behavior found by Malhotra et al. [35] and Malhotra and Woolf [36] for other series of compounds such as fluorinated ethers and alkan-2-one and by Cibulka et al. [24–26] for several compounds. Furthermore, the function $B(T)$ must be a decreasing function of temperature without a local minimum, in order to describe the increase in the isothermal compressibility with temperature along an isobar. This is due to the fact that the temperature dependence of the isothermal compressibilities, calculated from the Tait equation, is determined mainly by the temperature dependence of the parameter $B(T)$.

In the case of TrEGDME, we have found literature values at atmospheric pressure, due to Tovar et al. [37], and at 1 MPa, due to Conesa et al. [14], both at several temperatures; the deviations between our data and those from these references (Fig. 6) are less than 0.07 and 0.1 %, respectively.

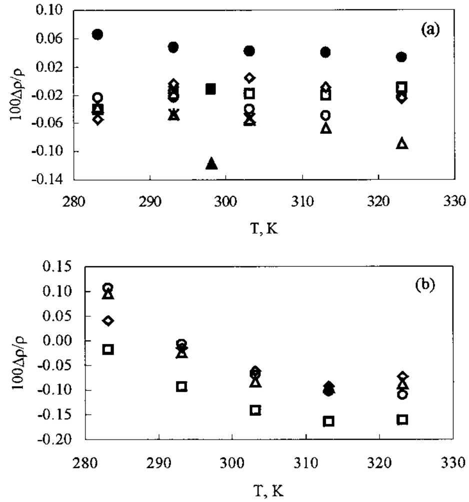

Fig. 6. Deviations of the density of the polyethers, $CH_3O–((CH_2)_2O)_n–CH_3$, between the literature and this work for $n = 3$ and $n = 4$ or the literature Tait correlation for $n = 1$ and $n = 2$ [39] versus the temperature. (a) 0.1 MPa: (●) $n = 4$ [37]; (○) $n = 4$ [38]; (×) $n = 4$ [11]; (△) $n = 3$ [37]; (□) $n = 2$ [40]; (■) $n = 2$ [43]; (▲) $n = 2$ [42]; (◇) $n = 1$ [37]. (b) 1 MPa [14]: (○) $n = 4$; (△) $n = 3$; (□) $n = 2$; (◇) $n = 1$.

For TEGDME (Fig. 6) there are some literature density data at normal pressure due to Tovar et al. [37], Esteve et al. [38], and Svejda et al. [11]. In these cases the deviations from our experimental values are less than 0.07, 0.05, and 0.05%, respectively. At 1 MPa, the deviations between our data and those of Conesa et al. [14] are less than 0.10%. In Fig. 6 we also represent, for other polyethylene glycol dimethylethers, the deviations from the correlation of Cibulka et al. [39] and the experimental data of Senger [12], Tovar et al. [37, 40], Treszczanowicz et al. [41, 42], and Serna et al. [43].

At high pressures, Cibulka et al. [39] determined the coefficients of Eqs. (6) and (7) by using the experimental density isotherm at 293.15 K of Svejda et al. [11], and, for this reason, their parameters C and B are independent of temperature. In order to compare our results with the correlation of Cibulka et al., we have determined the parameters of Eq. (5) by fitting the densities at normal pressure reported in the literature [11, 37, 38, 41]. The deviations between our experimental results and the obtained correlation are less than 0.07%, except for pressures and temperatures higher than 7 MPa and 323.15 K, where the deviations are slightly higher, due to the fact that B should be temperature dependent.

From Eq. (8), it is easy to obtain several derived functions. The isothermal compressibility, κ_T, is determined by:

$$\kappa_T = \left(\frac{1}{\rho}\right)\left(\frac{\partial\rho}{\partial p}\right)_T = \frac{C}{(1 + C\ln[(B(T)+p)/(B(T)+p_{\text{ref}})])(B(T)+p)} \tag{11}$$

The isobaric thermal expansion coefficient, α_p, is determined from its definition

$$\alpha_p = -\left(\frac{1}{\rho}\right)\left(\frac{\partial\rho}{\partial T}\right)_p \tag{12}$$

Finally, the internal pressure, $(\partial U/\partial V)_T$, is given by

$$\pi = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{13}$$

Values of π were obtained from the corresponding Tait equation, first by obtaining p as a function of T and ρ and then by performing the analytical differentiation of this expression.

Table V summarizes the isobaric thermal expansion coefficient, isothermal compressibilities, and internal pressure of both polyethers, calculated from Eqs. (11) to (13) with the parameters in Table IV. The estimated

Table V. Isobaric Thermal Expansion Coefficients, α_p, Isothermal Compressibilities, κ_T, and Internal Pressures, π, of TrEGDME and TEGDME

	p (MPa)										
	1	2	3	4	5	6	7	8	9	10	11
TrEGDME											
283.15 K											
α_p (10^{-4} K^{-1})	9.56	9.51	9.47	9.42	9.38	9.33	9.29	9.24	9.20	9.15	9.11
κ_T (10^{-4} MPa^{-1})	6.29	6.25	6.21	6.17	6.13	6.10	6.06	6.03	5.99	5.96	5.92
π (MPa)	430	429	429	428	428	427	427	426	426	425	425
293.15 K											
α_p (10^{-4} K^{-1})	9.72	9.67	9.61	9.57	9.52	9.47	9.42	9.37	9.33	9.28	9.23
κ_T (10^{-4} MPa^{-1})	6.72	6.68	6.64	6.60	6.56	6.52	6.49	6.45	6.41	6.37	6.34
π (MPa)	419	419	418	418	417	417	416	416	416	415	415
303.15 K											
α_p (10^{-4} K^{-1})	9.84	9.78	9.73	9.68	9.62	9.57	9.52	9.47	9.42	9.37	9.33
κ_T (10^{-4} MPa^{-1})	7.31	7.26	7.21	7.16	7.11	7.06	7.01	6.96	6.92	6.87	6.82
π (MPa)	407	406	406	406	405	405	405	404	404	404	403
313.15 K											
α_p (10^{-4} K^{-1})	9.93	9.87	9.81	9.76	9.70	9.65	9.59	9.54	9.49	9.44	9.39
κ_T (10^{-4} MPa^{-1})	7.88	7.82	7.76	7.70	7.64	7.59	7.53	7.48	7.42	7.37	7.32
π (MPa)	393	393	393	393	392	392	392	392	391	391	391
323.15 K											
α_p (10^{-4} K^{-1})	9.98	9.92	9.86	9.80	9.74	9.69	9.63	9.58	9.52	9.47	9.42
κ_T (10^{-4} MPa^{-1})	8.48	8.41	8.34	8.27	8.21	8.14	8.08	8.01	7.95	7.89	7.83
π (MPa)	379	379	379	379	379	379	378	378	378	378	378
TEGDME											
283.15 K											
α_p (10^{-4} K^{-1})	9.31	9.27	9.22	9.18	9.14	9.10	9.05	9.01	8.97	8.93	8.89
κ_T (10^{-4} MPa^{-1})	5.78	5.75	5.71	5.68	5.65	5.62	5.59	5.56	5.53	5.50	5.47
π (MPa)	455	455	454	453	453	452	452	451	451	450	450
293.15 K											
α_p (10^{-4} K^{-1})	9.24	9.20	9.15	9.11	9.06	9.02	8.98	8.93	8.89	8.85	8.81
κ_T (10^{-4} MPa^{-1})	6.23	6.19	6.15	6.12	6.08	6.04	6.01	5.97	5.94	5.91	5.87
π (MPa)	434	433	433	432	432	431	431	430	430	429	429

Table V. *(Continued)*

	p (MPa)										
	1	2	3	4	5	6	7	8	9	10	11
303.15 K											
α_p (10^{-4} K^{-1})	9.22	9.17	9.12	9.08	9.03	8.99	8.94	8.90	8.85	8.81	8.77
κ_T (10^{-4} MPa^{-1})	6.70	6.66	6.61	6.57	6.53	6.49	6.45	6.41	6.37	6.33	6.29
π (MPa)	416	416	415	415	414	414	413	413	413	412	412
313.15 K											
α_p (10^{-4} K^{-1})	9.24	9.19	9.14	9.10	9.05	9.00	8.96	8.92	8.87	8.83	8.79
κ_T (10^{-4} MPa^{-1})	7.18	7.13	7.08	7.03	6.99	6.94	6.89	6.85	6.80	6.76	6.71
π (MPa)	402	401	401	400	400	400	400	399	399	399	399
323.15 K											
α_p (10^{-4} K^{-1})	9.31	9.26	9.21	9.17	9.12	9.08	9.03	8.99	8.94	8.90	8.86
κ_T (10^{-4} MPa^{-1})	7.67	7.61	7.56	7.50	7.45	7.39	7.34	7.29	7.24	7.18	7.13
π (MPa)	391	391	391	391	391	391	391	391	390	390	390

uncertainties are $\pm 0.02 \times 10^{-3}$ K^{-1} and $\pm 0.05 \times 10^{-4}$ MPa^{-1}, respectively, for the two first properties and 1% for the last one.

With the goal of analyzing the dependence of these properties with the length of polyethylene glycol dimethylether, $CH_3O{-}((CH_2)_2O)_n{-}CH_3$, we have determined, with the help of the corresponding Tait correlations due to Cibulka et al. [39], the values of these three properties for MEGDME ($n = 1$) and DEGDME ($n = 2$). In Table II we report the isobaric thermal expansion coefficients α_p at normal pressure determined in this work, together with those of Tovar et al. [37] and of Esteve et al. [38], for TrEGDME ($n = 3$) and TEGDME ($n = 4$). We observe that our values are slightly higher than the others.

Figure 7 shows the trend of α_p with temperature at different pressures. This trend is more abrupt for the smaller polyether. α_p increases with temperature except in the case of TEGDME, for which the largest variation over the complete temperature range is 0.1×10^{-4} K^{-1}. At a constant temperature, α_p decreases with pressure and with the length of the polyether.

For TEGDME we have compared our values of the isothermal compressibilities with those of Svejda et al. [11] at 293.15 K and different pressures, obtaining a maximum deviation of 0.7%. The variations of this property with temperature, pressure, and length of the polyether are similar to those obtained for the isobaric expansivities (Fig. 8).

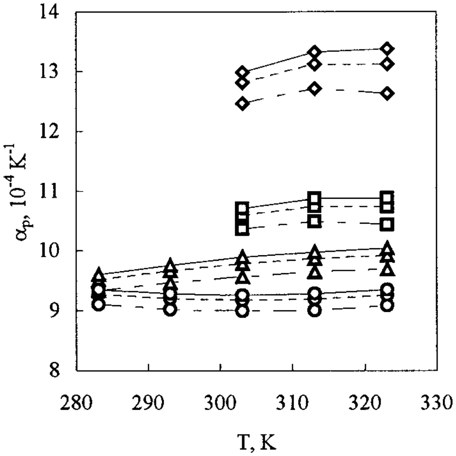

Fig. 7. Variation of the isobaric thermal expansion coefficient α_P with temperature at different pressures of $CH_3O–((CH_2)_2O)_n–CH_3$. (◇) $n = 1$; (□) $n = 2$; (△) $n = 3$; (○) $n = 4$. (—) 0.1 MPa; (···) 2 MPa; (– – –) 6 MPa.

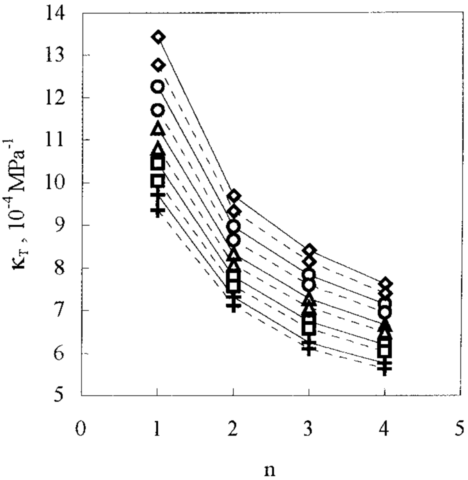

Fig. 8. Temperature and pressure dependence of the isothermal compressibility κ_T for different polyethylene glycol dimethylethers, $CH_3O–((CH_2)_2O)_n–CH_3$, versus n. (+) 283.15 K; (□) 293.15 K; (△) 303.15 K; (○) 313.15 K; (◇) 323.15 K. (—) 2 MPa; (···) 6 MPa.

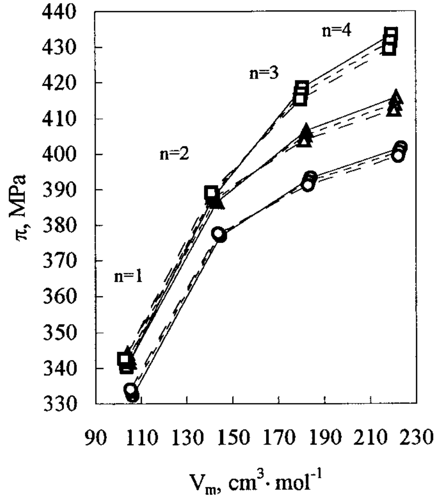

Fig. 9. Variation of the internal pressure, π, with the molar volume of the polyethylene glycol dimethylethers at different temperatures and pressures. (□) 293.15 K; (△) 303.15 K; (○) 313.15 K. (—) 2 MPa; (···) 6 MPa; (– – –) 10 MPa.

Finally, in Fig. 9 we present the behavior of the internal pressure, which is a quadratic function of temperature at constant volume for most liquids. For both polyethers, it is found that internal pressures decrease as the temperature increases or, in other words, cohesive forces [44] decrease with temperature. We also observe that the internal pressure increases with the length of the polyether. We note that the values of this property are quite large, and the changes with temperature, at constant volume, are relatively small. Moreover, the decrease in π when the molar volume decreases along an isobar is more important than the corresponding decrease in π along an isotherm. This tendency indicates that TrEGDME and TEGDME behave like an "associated" or "structured fluid" [45]. This is in agreement with the high values of the internal pressure and dipole moment [46] for both compounds. Similar behavior has been found by Malhotra and Woolf [47] for different families of polar liquids such as the ketones.

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REFERENCES

1. E. R. López, J. García, J. L. Legido, A. Coronas, and J. Fernández, *J. Chem. Soc. Faraday Trans.* **14**:2071 (1995).
2. E. R. López, J. García, A. Coronas, and J. Fernández, *Fluid Phase Equil.* **133**:229 (1997).
3. E. R. López, J. García, and J. Fernández, *J. Chem. Eng. Data* **44**:309 (1999).
4. G. Moncada Lo Giudice and F. Cotana, *Latest Developments of Researches on Fluids for Absorption Machines, Proc. CFCs, The Day After*, Padova, Italy (1994), p. 757.
5. U. Nowaczyk and F. Steimle, *Int. J. Refrig.* **15**:10 (1992).
6. U. Stüven, *Chem.-Ing.-Tech.* **6**:492 (1989).
7. D. Boer, M. H. Huor, M. Prevost, and A. Coronas, *International Absorption Heat Pump Conference*, ASME (1994), p. 483.
8. H. O. Spauschus, *Lubricants for Refrigeration Compressors: A 1996 Status Report, Bull. Int. Inst. Refrig.* **97**:3 (1997).
9. S. Y. Tserogounis and M. J. Riley, *AIChE* **40**:726 (1994).
10. G. D. Short, T. E. Rajewski, and J. E. Oberle, *Refrigerations Lubricants—Current Practice and Future Development, Proc. 1996 Int. Refrig. Conf. Purdue* (Purdue University, West Lafayette, IN, 1996), p. 265.
11. P. Svejda, M. A. Siddiqi, G. Hahn, and N. Christopher, *J. Chem. Eng. Data* **35**:47 (1990).
12. M. Senger, Ph.D. thesis (Heidelberg University, Heidelberg, Germany, 1994).
13. K. Sharipov and N. N. Bairamova, *Izv. Vyssh. Uchebn. Zaved. Neft Gaz.* **21**:62 (1978).
14. A. Conesa, S. Shen, and A. Coronas, *Int. J. Thermophys.* **19**:1343 (1998).
15. M.J. Lee, C.-K. Lo, and H. Lin, *J. Chem. Eng. Data* **43**:1076 (1998).
16. S. Matsuo and A. Van Hook, *J. Phys. Chem.* **88**:1032 (1984).
17. A. T. Sousa, C. A. Nieto de Castro, R. Tufeu, and B. Le Neindre, *High Temp.-High Press.* **24**:185 (1992).
18. B. Lagourette, C. Boned, H. Saint-Guirons, P. Xans, and H. Zhou, *Meas. Sci. Technol.* **3**:699 (1992).
19. L. A. Galicia-Luna, D. Richon, and H. Renon, *J. Chem. Eng. Data* **39**:424 (1994).
20. A. A. H. Pádua, J. M. N. A. Fareleira, J. C. G. Calado, and W. A. Wakeham, *J. Chem. Eng. Data* **41**:1488 (1996).
21. A. M. Demiriz, Ph.D. thesis (University of Bochum, Bochum, Germany, 1986).
22. *TRC Thermodynamics Tables* (Texas A&M University, College Station, 1997).
23. A. Compostizo, A. Crespo Colin, M. R. Vigil, R. G. Rubio, and M. Diaz Peña, *J. Phys. Chem.* **92**:3998 (1988).
24. I. Cibulka and L. Hnědkovský, *J. Chem. Eng. Data* **41**:657 (1996).
25. I. Cibulka and T. Takagi, *J. Chem. Eng. Data* **44**:411 (1999).
26. I. Cibulka and M. Zirková, *J. Chem. Eng. Data* **39**:876 (1994).
27. M. J. Assael, J. H. Dymond, and D. Exadaktilou, *Int. J. Thermophys.* **15**:155 (1994).
28. R. Malhotra and L. A. Woolf, *J. Chem. Thermodyn.* **23**:49(1991).
29. H. Kashiwagi, T. Hashimoto, Y. Tanaka, H. Kubota, and T. Makita, *Int. J. Thermophys.* **3**:210 (1982).
30. A. T. Sousa, Ph.D. thesis (University of Lisbon, Lisbon, Portugal, 1994).

31. R. Malhotra and L. A. Woolf, *J. Chem. Thermodyn.* **20**:603 (1988).
32. J. Hruby, J. Klomfar, and O. Sifner, *J. Chem. Thermodyn.* **25**:1229 (1993).
33. R. R. Tillner and H. D. Baehr, *J. Chem. Thermodyn.* **25**:277 (1993).
34. G. Morrison and D. K. Ward, *Fluid Phase Equil.* **62**:65 (1991).
35. R. Malhotra, W. A. Van Hook, and L. A. Woolf, *Int. J. Thermophys.* **16**:111 (1995).
36. R. Malhotra and L. A. Woolf, *J. Chem. Thermodyn.* **28**:1411 (1996).
37. C. A Tovar, E. Carballo, C. A. Cerdeiriña, and L. Romaní, *J. Chem. Eng. Data* **42**:1085 (1997).
38. X. Esteve, F. Olivé, K. R. Patil, S. K. Chaudhari, and A. Coronas, *Fluid Phase Equil.* **110**:369 (1995).
39. I. Cibulka, L. Hnědkovský, and T. Takagi, *J. Chem. Eng. Data* **42**:2 (1997).
40. C. A Tovar, E. Carballo, C. A. Cerdeiriña, M. I. Paz Andrade, and L. Romaní, *Fluid Phase Equil.* **136**:223 (1997).
41. T. Treszczanowicz, G. C. Benson, and B. C.-Y. Lu, *J. Chem. Eng. Data* **33**:379 (1988).
42. T. Treszczanowicz, C. L. Halpin, and G. C. Benson, *J. Chem. Eng. Data* **27**:321 (1982).
43. A. Serna, I. García de la Fuente, J. A. González, and J. C. Cobos, *Fluid Phase Equil.* **133**:187 (1997).
44. J. H. Hildebrand and R. L. Scott, *Solubility of Non-electrolytes* (Reinhold, New York, 1950).
45. A. F. M. Barton, *J. Chem. Educ.* **48**:156 (1971)
46. K. Kimura and R. Fujishiro, *Bull. Chem. Soc. Jpn.* **39**:608 (1966).
47. R. Malhotra and L. A. Woolf, *J. Chem. Thermodyn.* **24**:1207 (1992).