J. Chem. Eng. Data **2005,** *50,* 1667−1671

Compressed Liquid Densities and Saturated Liquid Densities of Dimethyl Ether (RE170)

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Dimethyl ether (RE170) is a very important chemical compound, largely employed in the chemical industry, but the available literature data for this fluid, especially in terms of liquid density, are scarce. In this paper, compressed liquid density data were measured along eight isotherms between (283.15 and 353.15) K up to 35 MPa with a vibrating tube densimeter (Anton Paar DMA 512) and, on the basis of these data, the saturated liquid densities were estimated. The overall estimated uncertainty for the density data is within ± 0.1 %. The experimental compressed liquid density data and the estimated saturated density data were correlated by means of fitting equations that are also presented in this paper.

Introduction

PVT measurements are particularly important to describe the thermodynamic behavior of fluids. Dimethyl ether (RE170) is an important fluid used in several industrial applications, as a refrigerant, aerosol propellant, solvent, fuel additive, and extraction agent. But few experimental data are available in the literature. Most of them were published several years ago regarding, for example, the RE170 saturated density, vapor pressure, and surface tensions.[1−5] While a few data were recently published on viscosity of the saturated liquid,[6] surface tension,[7] vapor pressure,[8] critical parameters, and saturated density.[9] However, compressed liquid density data are still lacking. For this reason, compressed liquid density data are reported here for this fluid along eight isotherms between (283.15 and 353.15) K up to 35 MPa.

Very accurate data were obtained by means of an apparatus based on a vibrating tube densimeter. The estimated temperature uncertainty is ± 0.02 K and ± 20 kPa in terms of pressure. The maximum uncertainty in the measured densities (ρ) is estimated to be ± 0.6 kg·m^{-3}.

Moreover, saturated liquid densities were estimated by extrapolating isothermal compressed liquid density data up to the saturated pressure and compared with the available literature data.[9] The second aim of this study was to correlate the experimental $P\rho T$ data for both the compressed liquid and the saturated liquid density.

Experimental Section

Materials. RE170 was supplied by Aldrich, with a declared purity >99 %. No impurities were detected by gas chromatography using both flame ionization (FID) and thermal conductivity (TCD) detectors. To eliminate the non-condensable gases, the sample underwent several cycles of freezing with liquid nitrogen, evacuation, thawing, and ultrasound.

Experimental Apparatus. The compressed liquid density data were measured using an apparatus based on a stainless steel vibrating U-tube (Anton Paar DMA 512) already described in ref 10. A scheme of this apparatus is shown in Figure 1. These kinds of measurements are based on the evaluation of the vibrating period (π) of a hollow resonating tube filled with the fluid to be studied, as a function of pressure P and temperature T. By means of a proper calibration, this period can be converted into density.

The densimeter was connected to an electronic evaluation unit for the measurement of the oscillation period (Anton Paar mPDS 2000) and filled with the sample by means of a circuit of stainless steel tubes connecting the cell to the pure refrigerant bottle. The fluid was pressurized into the vibrating tube by means of a manual piston pump (RUSKA T1200V). Pressure was measured through a differential pressure gauge (Druck DPI 145) with a scale-up to 35 MPa. The uncertainty in the pressure measurement was estimated to be within ± 20 kPa.

The temperature of the vibrating tube was stabilized by a circulating water coming from an external thermostated bath, through a heat exchanger surrounding the U-tube, reaching a stability of ± 0.003 K all along the measurements. A thermal regulator allowed fine local temperature regulation around the connection with the circuit by means of an electrical heating resistance fed by a variable transformer. This ensured temperature and density uniformity inside the vibrating tube by reducing the heat flux among the connecting tubes. The temperature was measured by a PT 100 Ω resistance thermometer, and the estimated uncertainty in the temperature measurement is within ± 0.02 K.

A dedicated software, developed in the LabView 5.1.1 environment, allows the continuous acquisition, visualization, and elaboration of the main experimental parameters (period, temperature, and pressure). An equation of state (EoS) for the calibration fluid and the proper calibration

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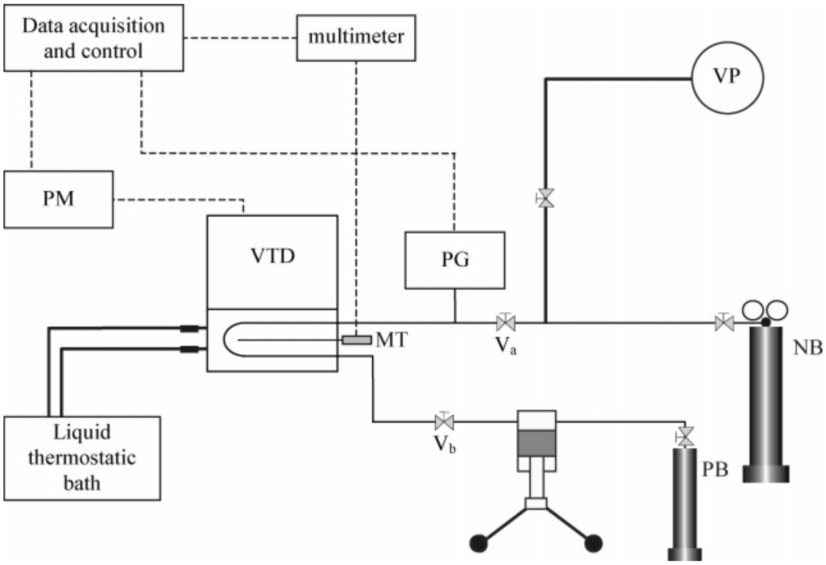

Figure 1. Density measurements apparatus scheme. MPP, manual piston pump; MT, temperature measurements sensor; NB, nitrogen bottle; PB, pure refrigerant bottle; PG, pressure gauge; PM, frequency meter; V_a and V_b, valves; VP, vacuum pump; VTD, vibrating tube densimeter.

equation are also implemented into the software to allow the online calculation of the experimental density.

Experimental Procedures. After purging the circuit by flowing nitrogen and putting it under vacuum overnight, valve V_a was closed and the U-tube was filled with the sample. The fluid was introduced into the circuit by opening all valves between the sample cylinder (PB) and valve V_a. Then the fluid was pressurized to around 35 MPa by running the manual piston pump (MPP), and valve V_b was closed. After the temperature has stabilized, valve V_b was slightly opened, and controlled bleeding was created through it. Then the fluid slowly flowed from the measuring circuit to the MPP, where some free volume was prevoiously created by displacing the piston. As a consequence, pressure continuously decreased inside the vibrating tube densimeter cell at a rate of about 10 kPa/s till a discontinuity was observed revealing the vapor phase formation. At this point, the liquid-density isotherm was completed, the fluid could be recompressed inside the circuit, and after changing the experimental temperature, it was possible to measure a new isotherm. All along this process, pressures and periods were continuously recorded by the data acquisition system.

To avoid any vapor bubble in the circuit disturbing the measurement, the minimum pressure that can be achieved in the circuit corresponds to the saturation pressure of the fluid at the higher temperature between the measuring and ambient temperatures.

The densimeter was calibrated by measuring the oscillation period of the U-tube under vacuum and filled with a fluid of known density. The measured oscillation period π was correlated to the known density of water at six different pressures regressing the coefficients ϕ, φ, γ, and B in the following calibration equation, applied at constant temperature:

$$\pi^2 = (\phi P^2 + \varphi P + \gamma)\rho + B \tag{1}$$

where π is the oscillation period in μs, P is the calibration pressure in kPa, and ρ is the density in kg/m^3. Water was used as the calibration fluid. The equation proposed by Wagner and Pruss[11] was used to determine the water density at the calibration pressure and temperature.

Table 1. Total Uncertainty in the Density Measurements

Uncertainty of Pressure Measurements in kPa	
uncertainty of the pressure gauge	± 20
stability	± 3
total	± 23
Uncertainty of Temperature Measurements in K	
uncertainty of thermometer	± 0.020
stability of the thermostatic bath	± 0.003
total	± 0.023
Uncertainty of Period of Oscillation Measurements in μs	
variation	0.020
uncertainty in counter	0.001
total	0.021
Uncertainty of the Calibration eq 1 in kg·m^{-3}	
uncertainty of the equation of state	0.14
influence of period of oscillation fluctuations under vacuum	0.10
deviation from the eq 1	0.10
total	0.34
Uncertainty in Density Calculation in kg·m^{-3}	
uncertainty in pressure measurements	0.10
uncertainty in temperature measurements	0.10
uncertainty in period of oscillation measurements	0.10
uncertainty of the calibration equation	0.34
total	0.64

The total estimated uncertainty of this apparatus, evaluated taking into account the influence of temperature, pressure, period of oscillation, and water EoS uncertainties, is around 0.6 kg/m^3 as shown in Table 1.

To check the of the vibrating tube densimeter technique, a few density measurements for the pentafluoroethane (R125) were performed at (283.15, 303.15, 323.15, and 353.15) K from the saturation pressure to 350 bar. In fact, an accurate EoS is available to describe its thermodynamic properties. The deviations between the experimental data and the calculated data using the database Refprop 7.0[12] (for which a very accurate Helmholtz EoS is available) are shown in Figure 2. In the present experimental temperature range, the deviations are within ± 0.1 % for this fluid.

Results and Discussion

Compressed Liquid Density. The main aim of this study is to produce new data for the compressed liquid density of the RE170. 21388 compressed liquid density

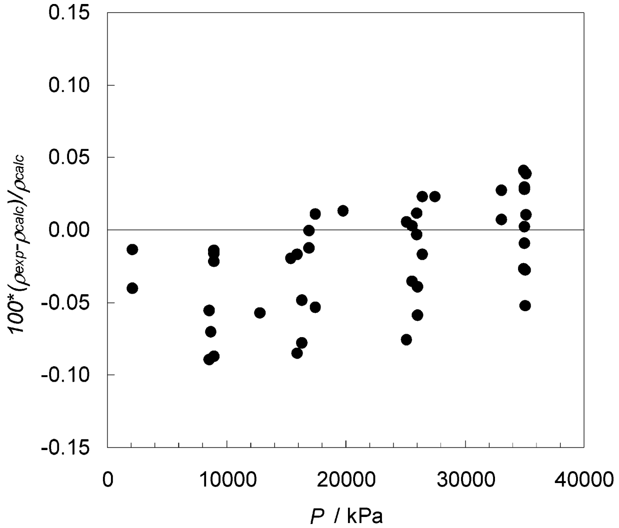

Figure 2. Compressed liquid density deviations for R125 from the Refprop database 7.0.[12]

Table 2. Experimental Compressed Liquid Density for RE170

T	P	ρ	T	P	ρ	T	P	ρ
K	kPa	kg·m³	K	kPa	kg·m³	K	kPa	kg·m³
283.16	35521	729.5	313.15	35404	696.2	343.16	35240	661.7
283.14	32151	726.1	313.15	32000	692.0	343.15	32018	656.5
283.15	29056	722.8	313.14	29291	688.3	343.14	29042	651.5
283.15	25006	718.2	313.15	25629	683.2	343.15	25025	644.3
283.14	21845	714.6	313.15	21159	676.6	343.15	21209	636.9
283.14	18086	710.2	313.15	19082	673.3	343.15	18017	630.0
283.15	14790	705.9	313.15	15041	666.5	343.15	15026	623.1
283.14	11009	700.8	313.15	11057	659.2	343.15	12026	615.4
283.14	9016	698.0	313.15	9070	655.3	343.15	11043	612.6
283.14	5003	692.0	313.15	5011	646.6	343.15	8077	603.7
283.14	2513	688.1	313.14	2207	639.8	343.15	5002	593.1
283.15	550	684.8	313.15	1003	636.8	343.15	3041	585.3
293.16	34680	717.5	323.15	35338	684.8	353.15	35513	650.1
293.15	32201	714.8	323.14	32540	680.9	353.15	32599	645.3
293.15	29096	711.3	323.15	29643	676.8	353.15	29020	638.6
293.15	25071	706.5	323.14	26052	671.4	353.14	25005	630.8
293.15	21007	701.4	323.14	23929	667.9	353.14	22764	625.8
293.15	18059	697.4	323.15	20934	663.1	353.15	21002	622.2
293.15	15028	693.2	323.14	17659	657.5	353.14	18102	615.2
293.15	11056	687.3	323.15	15253	652.9	353.15	15245	607.6
293.15	9039	684.2	323.14	10877	643.9	353.15	11065	594.9
293.15	5017	677.4	323.14	7033	634.9	353.15	9548	589.9
293.15	2506	672.9	323.14	4998	629.7	353.15	8162	584.8
293.15	602	669.3	323.14	1750	620.4	353.15	7284	581.4
303.16	35012	707.1	333.15	35361	673.2			
303.15	32101	703.7	333.15	31963	668.2			
303.16	29118	700.0	333.15	29204	663.9			
303.16	25625	695.5	333.15	25004	657.1			
303.16	21216	689.5	333.15	20991	649.8			
303.15	19009	686.3	333.15	16998	642.0			
303.15	15007	680.1	333.15	14097	635.6			
303.16	11000	673.6	333.15	11059	628.5			
303.15	9000	670.1	333.15	9001	623.3			
303.16	5002	662.5	333.15	6504	616.3			
303.16	2502	657.3	333.15	3523	606.9			
303.15	804	653.8	333.15	1545	600.4			

values were measured at isothermal conditions in the temperature range from (283 to 353) K and pressure up to 35 MPa. A selection of these data are summarized in Table 2. Figure 3 shows their distribution on a (ρ, P) plane. All the measured data are available in the Supporting Information on the Web as explained at the end of the paper.

All of the experimental data in the temperature range between (283.15 and 343.15) K were correlated with a generalized Tait equation in the form[13]

$$1/\rho = 1/\rho_{\mathrm{sat}}\left(1 - c \ln \frac{\beta + P}{\beta + P_{\mathrm{sat}}}\right) \tag{2}$$

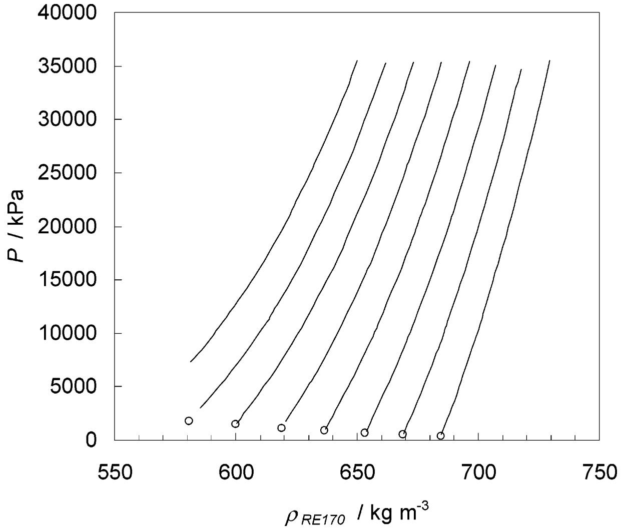

Figure 3. Distribution of the experimental compressed liquid density data (—) and of the estimated saturated liquid density data (○) for RE170.

Table 3. Coefficients of the Generalized Tait Equation for the RE170

coefficient	numerical value	coefficient	numerical value
a	−0.97189	f	4.89854
b	41.43544	g	0.41419
c	0.09314	h	1.32702
d	−135.58828	j	0.09144
e	154.26766	k	0.00829

where ρ is the molar density (mol/m³), ρ_{sat} is the estimated saturated molar density, P is the pressure (kPa), and P_{sat} is the vapor pressure[12−14] at a given temperature. In fact, it is worth noting that during the measurements, some problems in the temperature stability were found near the saturation pressure at 353.15 K. For this reason, the saturated molar volume was not estimated at this temperature, as indicated below, and the data corresponding to this isotherm are presented in this paper but not considered in the regression.

The β and c parameters in eq 2 were obtained from the following equations:

$$\beta = P_{\mathrm{c}}[-1 + a(1 - T_{\mathrm{r}})^{1/3} + b(1 - T_{\mathrm{r}})^{2/3} + d(1 - T_{\mathrm{r}}) + e(1 - T_{\mathrm{r}})^{4/3}] \tag{3}$$

$$e = \exp(f + g\omega + h\omega^2) \tag{4}$$

$$c = j + k\omega \tag{5}$$

where the reduced temperature $T_{\mathrm{r}} = T/T_{\mathrm{c}}$ and ω is the acentric factor calculated through the basic equation:

$$\omega = -\log_{10}P_{\mathrm{rsat(at}\ T_r\,=\,0.7)} - 1 = 0.2007 \tag{6}$$

where $P_{\mathrm{rsat(at}\ T_r\,=\,0.7)}$ is the reduced vapor pressure at the reduced temperature $T_{\mathrm{r}} = 0.7$.

The following values of critical properties were used:[12−14]

$$T_{\mathrm{c}} = 400.10\ \mathrm{K}$$

$$P_{\mathrm{c}} = 5370\ \mathrm{kPa}$$

The a−k coefficients, regressed from the experimental data, are given in Table 3.

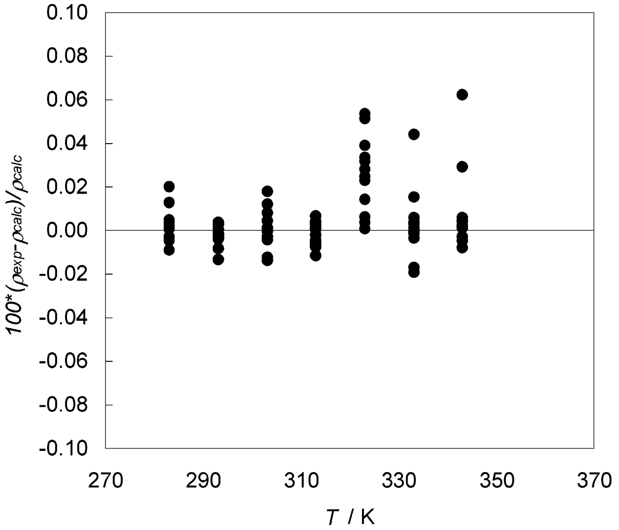

Figure 4. Deviations of the experimental liquid compressed density data for RE170 from the Tait eq 2.

Table 4. Saturated Liquid Density Data of the RE170

T / K	P_{sat} / kPa	ρ_{sat} / kg·m^{-3}	T / K	P_{sat} / kPa	ρ_{sat} / kg·m^{-3}
283.15	371	684.5	323.15	1139	618.9
293.15	506	669.1	333.15	1444	600.0
303.15	676	653.4	343.15	1806	580.7
313.15	885	636.6			

Table 5. Coefficients of Equation 7

A	B	C	D
−0.80683	2.36608	0.19907	−0.83569

The deviations between the Tait equation and the experimental data are shown in Figure 4. This equation is able to represent the experimental density data with an absolute average deviation (AAD) of 0.02 % and a maximum deviation of 0.06 %. Moreover, this regressed equation is able to extrapolate the compressed liquid density data at 353.15 K with an AAD of 0.16 %, with a maximum deviation of 0.3 %.

Saturated Liquid Density. The saturated density data for RE170 were calculated extrapolating each isotherm between (283.15 and 343.15) K to the vapor pressure using a third degree polynomial, in the form $\rho = a_0 + a_1P + a_2P^2 + a_3P^3$.

The vapor pressures were determined by means of Refprop 7.0.[12−14] The values at saturation are reported in Table 4 and included in Figure 3 (empty circles).

Then the saturated liquid density data (ρ_{sat} is in kg/m^3) were correlated with the following equation:[15]

$$\rho_{sat} = \rho_c(1 + A\tau^{1/3} + B\tau^{2/3} + C\tau + D\tau^{4/3}) \qquad (7)$$

where

$$\tau = 1 - \frac{T}{T_c} = 1 - T_r$$

and the critical density $\rho_c = 488$ kg/m^3.[12−14]

The parameters of eq 7 are reported in Table 5. The absolute average deviation between eq 7 and the extrapolated saturated liquid densities is ± 0.03 %, and the deviations are shown in Figure 5.

With eq 7, a comparison with the available literature data[9] in the considered temperature range was performed over the experimental temperature range, and the results are shown in Figure 5. The AAD between eq 7 and the literature data[9] is 0.2 % in terms of density. Wu et al.[9] proposed an equation to estimate the saturated liquid density, but, unfortunately, we were not able to reproduce their data using the published equation. Probably, the reported parameters are not correct. Data from Maass and Boomer[1] were not considered since they are out of the experimental temperature range.

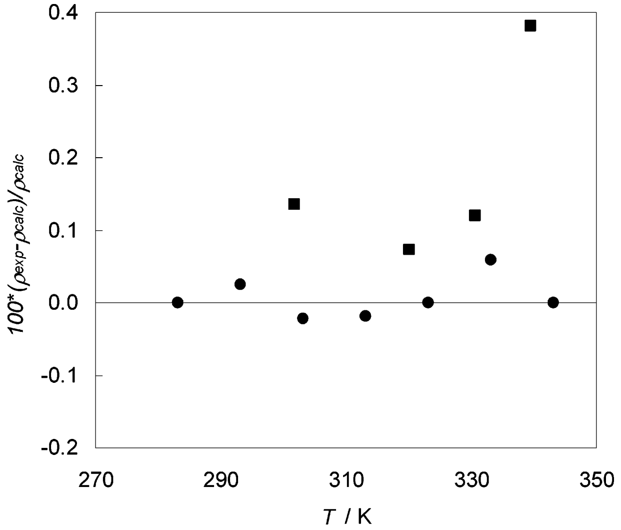

Figure 5. Deviations of RE170 saturated liquid density data from eq 7. ●, this work; ■, Wu et al.[9]

Conclusions

Compressed liquid density data for the dimethyl ether (RE170) were determined along eight isotherms in the temperature range between 283.15 K and 353.15 K. Our experimental data (except the isotherm at 353.15 K) were used to regress the parameters of a Tait equation. The AAD between the model (eq 2) and the experimental results was of about ± 0.02 %, with a maximum deviation of 0.06 %. The saturated liquid density was calculated at the experimental temperatures between 283.15 K and 343.15 K by extrapolating the liquid density isotherms to the vapor pressures. The saturated liquid densities were correlated with a four-parameter equation in the reduced form that could represent the saturated density data with an AAD of 0.02 %. Higher deviations were observed between this equation and the saturated density literature data.[9]

Supporting Information Available:

All experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review April 7, 2005. Accepted June 27, 2005.

JE050135Q