

# Densities of Liquid and Supercritical Mixtures of Methyl Myristate and Carbon Dioxide at High Pressures

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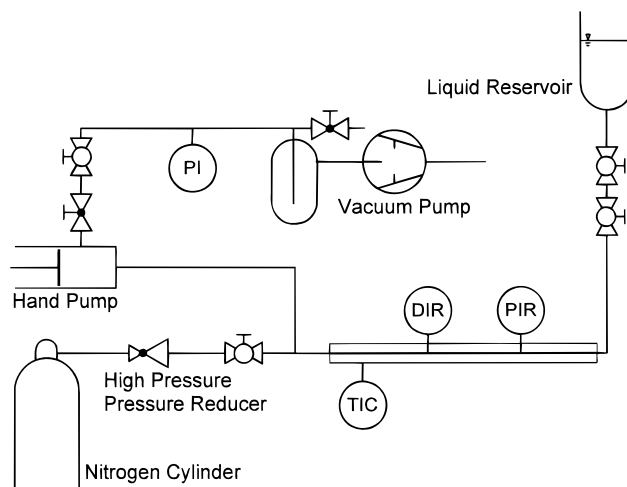
Densities of liquid mixtures of methyl myristate (tetradecanoic acid methyl ester:  $\text{CH}_3\text{OOC}(\text{CH}_2)_{12}\text{CH}_3$ , here abbreviated as MM) and carbon dioxide ( $\text{CO}_2$ ) were measured at temperatures of 40 °C, 50 °C, and 60 °C and pressures of 1 bar to 170 bar for compositions from pure MM to the saturated MM +  $\text{CO}_2$  liquid phase. Some mixtures were compressed above their critical point. The accuracy of the measurements is estimated to be  $\pm 0.3 \text{ kg/m}^3$  for density,  $\pm 0.1 \text{ bar}$  for pressure, and  $\pm 0.1 \text{ K}$  for temperature. Even at high mole fractions of carbon dioxide, the densities showed liquidlike behavior. At constant composition and constant temperature, the density of the mixture increases linearly with pressure. At higher mole fractions of carbon dioxide, the slope of these linear functions increases significantly. Together with already published equilibrium-composition data, the results allow an online determination of liquid-phase compositions from measured density, pressure, and temperature.

## Introduction

At high pressures carbon dioxide ( $\text{CO}_2$ ) is significantly soluble in methyl myristate (tetradecanoic acid methyl ester:  $\text{CH}_3\text{OOC}(\text{CH}_2)_{12}\text{CH}_3$ , here abbreviated as MM), which has considerable effects on the properties of the liquid phase. So far only densities of pure MM and its saturated mixture with carbon dioxide have been reported (Lockemann, 1994a,b). From the thermodynamic point of view, the behavior of unsaturated mixtures is interesting also. Density could provide a rapid method to determine online phase compositions at high pressures, because of the development of high-resolution density measurement devices. Equilibrium compositions are known through the work of Inomata et al. (1989) and Lockemann (1994a,b). Additional properties of the saturated mixtures that have been measured include viscosities (Lockemann, 1994a; Lockemann and Schlünder, 1995), diffusion coefficients (Lockemann 1994a; Lockemann and Schlünder, 1996), and interfacial tensions (Lockemann, 1994a,c). Properties at high pressures of unsaturated mixtures are so far not known.

## Experimental Section

**Calibration and Measurement on the Pure Substances.** Density measurements on the pure substances were performed with a high-pressure experimental setup as shown in Figure 1. It was also used to calibrate the high-pressure density-measuring equipment DMA 512 P from Anton Paar (Graz/Austria) with nitrogen and water at temperatures of 40 °C, 50 °C, and 60 °C at pressures of 1, 10, 20, 30, ..., 170 bar. The main parts of the setup are a vacuum pump, a hand pump, a high-pressure gas inlet, a pressure transducer, a liquid reservoir, and the density-measuring equipment. The vacuum pump was used to evacuate the entire setup to pressures below 0.1 mbar in order to remove remaining gas. The vacuum is controlled through a vacuum transducer from Leybold (Köln/Germany). The internal volume of the high-pressure part of the setup can be very finely adjusted with the hand pump (Universität Kaiserslautern/Germany), so that the desired



**Figure 1.** Calibration of the density-measuring device and density measurement of pure substances.

pressure can be regulated accurately. While liquids are examined, the pressure is adjusted only with the hand pump. For gas measurements the high-pressure pressure reducer from AGA (Stuttgart/Germany) serves for coarse control and the hand pump for fine control. The temperature of the densimeter sensor and its high-pressure supply pipes is constant with  $\pm 0.01 \text{ K}$  and adjusted with  $\pm 0.05 \text{ K}$  accuracy. The temperature sensor is a platinum resistance thermometer from Heräus (Hanau/Germany) calibrated at PTB. Its resistance was measured with an ohmmeter from Solartron (München/Germany). The temperature control is monitored with calibrated thermocouples. The system pressure is measured with a pressure transducer from Burster (Gernsbach/Germany). It is used with an analogue output with a resolution of 0.01 bar and a manufacturer guaranteed accuracy of  $\pm 0.5\%$ , which was improved through tempering and calibrating with a pressure balance model 5501 from Desgranges & Huot (Rodgau/Germany) from 1 bar to 80 bar with an uncertainty of less than  $\pm 0.1 \text{ bar}$ . The substances used were obtained from the following suppliers: pentane (99.5%) and MM (99%) from Merck

**Table 1. Densities of MM + CO<sub>2</sub> Mixtures at 40 °C,  $\rho/\text{kg m}^{-3}$** 

pressure <i>P</i> /bar	equilibrium pressure <i>P</i> <sup>*</sup> /bar															
	1	10	20	30	40	50	60	70	75	80	82	85.1	87.4	89.9	90	
1	852.20															
10	852.87	855.71														
20	853.55	856.57	859.93													
30	854.25	857.33	860.79	864.05												
40	854.94	858.06	861.60	864.99	868.08											
50	855.62	858.80	862.40	865.88	869.10	872.17										
60	856.30	859.53	863.22	866.74	870.07	873.35	875.91									
70	856.95	860.27	863.99	867.62	871.04	874.45	877.26	878.70								
75									879.01							
80	857.62	860.98	864.76	868.49	872.00	875.53	878.57	880.30		877.74						
82											875.69					
85.1												871.16				
87.4													860.08			
89.9														840.46		
90	858.28	861.67	865.52	869.32	872.93	876.60	879.80	881.83		880.06						837.35
100	858.94	862.42	866.28	870.13	873.88	877.66										
110	859.58															
120	860.23															
130	860.87															
140	861.51															
150	862.14															
160	862.76															
170	863.39															

**Table 2. Densities of MM + CO<sub>2</sub> Mixtures at 50 °C,  $\rho/\text{kg m}^{-3}$** 

pressure <i>P</i> /bar	equilibrium pressure <i>P</i> <sup>*</sup> /bar														
	1	10	20	30	40	50	60	70	80	90	95	100	105	110	
1	844.68														
10	845.36	847.67													
20	846.10	848.55	850.93												
30	846.83	849.33	851.81	854.07											
40	847.55	850.11	852.64	855.06	857.12										
50	848.26	850.89	853.47	855.95	858.11	860.22									
60	848.97	851.62	854.31	856.84	859.15	861.37	863.00								
70	849.68	852.34	855.14	857.72	860.09	862.47	864.26	865.21							
80	850.38	853.12	855.91	858.65	861.03	863.51	865.46	866.67	866.72						
90	851.08	853.85	856.75	859.48	862.02	864.55	866.66	868.03	868.30	866.03					
95											864.49				
100	851.77	854.57	857.53	860.38	862.96	865.60	867.86	869.34	869.92	868.07		861.80			
105													855.94		
110	852.45	855.31	858.30	861.21	863.90	866.59	869.01	870.70	871.43	870.07					848.19
120	853.12														
130	853.79														
140	854.46														
150	855.14														
160	855.79														
170	856.45														

(Darmstadt/Germany), carbon dioxide (99.995%) and nitrogen (99.996%) from Messer-Griesheim (Hohenbrunn/Germany), double-distilled water with conductivity of ISO-grade 2 (Universität Karlsruhe (TH)/Germany), i.e.,  $\leq 0.1$  mS/m at 25 °C.

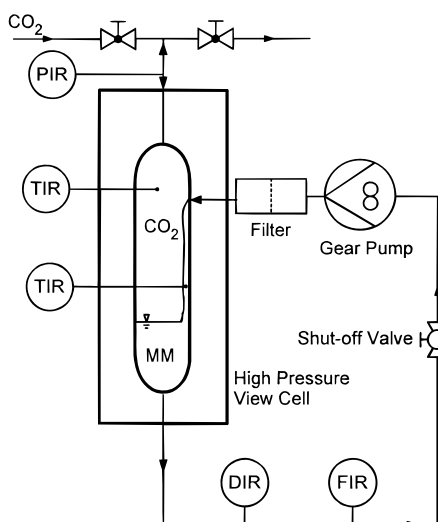
The density-measuring equipment is an oscillating tube densimeter. For its calibration at each desired pressure and temperature, two substances with known densities are needed. To be able to measure mixture compositions later, high accuracy has to be achieved because density is not a strong function of composition. Not many substances with precisely known densities at high pressures do exist. Water and nitrogen were used to calibrate the densimeter, and pentane was used to check the calibration because of their availability in high purity. Densities of water were obtained from the IAPWS equation of state from Pruss and Wagner (1997) with a Fortran program of the Institut für Thermo- und Fluidodynamik of the Ruhr-Universität Bochum (Germany). Nitrogen densities were calculated with the equation of state from Span and Wagner (1993). To calibrate with water the setup was evacuated and filled with degassed, double-distilled water through the liquid

reservoir. For the nitrogen calibration the setup was evacuated and flushed several times. The densimeter was plurally calibrated for each temperature (40, 50, 60 °C) and every pressure (1, 10, 20, 30, ..., 0.170 bar) with a resolution of 0.05 to 0.005 kg/m<sup>3</sup>. Then the calibrated densimeter was used to examine pentane, to obtain the accuracy of the measuring system. The comparison with densities from the equation of state of Kratzke et al. (1985) yields an accuracy of  $\pm 0.25$  kg/m<sup>3</sup>. Then the densities of pure MM were determined analogously. MM is not stable at high temperatures, and extrapolation of equilibrium data made vacuum degassing seem to be not necessary. The densities of pure MM are given in Tables 1, 2, and 3 in their second columns ( $P^* = 1$  bar). The densities show a linear increase with pressure which is almost the same for the three temperatures. The increase of density  $\rho$  with pressure  $P$  at constant temperature  $T$  and constant composition (mole fraction of CO<sub>2</sub>:  $x$ ) is here called the compression factor  $K = (\partial\rho/\partial P)_{T,x}$ .

**Measurement on the Mixtures.** The setup for measuring liquid and supercritical mixtures is shown in Figure 2. Its central part is a high-pressure view cell, which has an

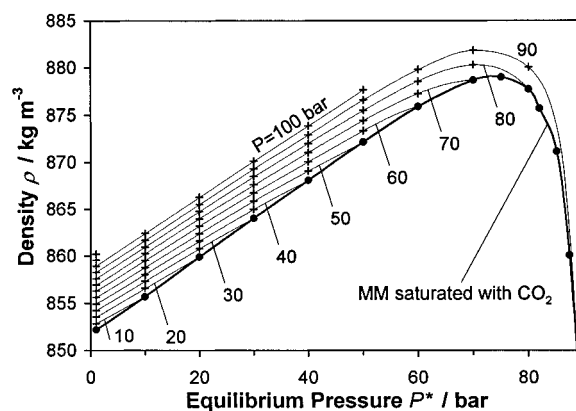
**Table 3.** Densities of MM + CO<sub>2</sub> Mixtures at 60 °C,  $\rho/\text{kg m}^{-3}$ 

pressure $P/\text{bar}$	equilibrium pressure $P^*/\text{bar}$													
	1	10	20	30	40	50	60	70	80	90	100	105	110	
1	836.98													
10	837.71	839.19												
20	838.50	840.08	841.92											
30	839.29	840.92	842.81	844.45										
40	840.05	841.75	843.71	845.38	846.86									
50	840.82	842.54	844.54	846.38	847.91	849.06								
60	841.60	843.38	845.38	847.27	848.90	850.22	851.17							
70	842.36	844.16	846.26	848.20	849.89	851.26	852.37	852.84						
80	843.09	844.94	847.15	849.15	850.83	852.26	853.57	854.26	854.36					
90	843.84	845.72	847.93	850.04	851.83	853.40	854.73	855.56	855.83	854.93				
100	844.56	846.50	848.76	850.92	852.77	854.45	855.87	856.82	857.29	856.60	854.45			
105												853.60		
110	845.29	847.23	849.59	851.80	853.70	855.49	857.02	858.07	858.76	858.28				852.23
120	846.00													
130	846.70													
140	847.41													
150	848.12													
160	848.81													
170	849.48													

**Figure 2.** Density measurement of MM + CO<sub>2</sub> mixtures.

inner volume of about 120 mL and is immersed in a tempered water bath. The temperature is constant with  $\pm 0.01$  K and adjusted with  $\pm 0.05$  K. The densimeter, the pressure transducer, and the thermocouples are the same as described above. The view cell serves as the contact area for MM and CO<sub>2</sub>. The system pressure is controlled by adding CO<sub>2</sub>. The liquid phase is circulated with a gear pump from Micropump (Concord/United States) almost without pulsation until phase equilibrium at temperature and pressure is reached. Equilibrium is detected by constancy of density and pressure. This pressure is the equilibrium pressure  $P^*$  and a measure for the amount of CO<sub>2</sub> in MM. With equilibrium data from Lockemann (1994a,b) and Inomata et al. (1989), the equilibrium pressure can be converted into liquid-phase composition. The pump head and a part of its drive is entangled with the copper tube and then isolated. Tempered water flows through the copper tubes. All high-pressure tubes outside the water bath are tempered by outer tubes with circulating water and isolated.

When phase equilibrium is reached, the shut-off valve in the liquid-phase circuit is closed, the gear pump is switched off, and density measurement begins. The system pressure can be increased and controlled by introduction of further CO<sub>2</sub>, whereby the sample in the densimeter is compressed at constant composition. The supply pipes are

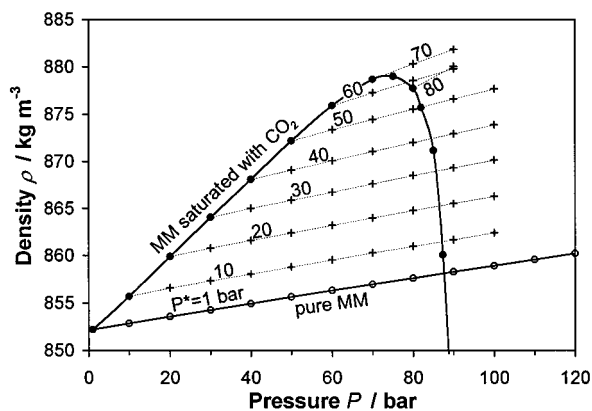
**Figure 3.** Isobaric densities of MM + CO<sub>2</sub> mixtures at 40 °C.

by far long enough that no change of the sample composition occurs owing to diffusion of CO<sub>2</sub> or free convection. This was ensured by measuring an isostere conversely, starting with highest pressure. Even an hour after the end of measuring an isostere no density change could be observed. Measurement reproducibility within a few hours was  $\leq 0.05$  kg/m<sup>3</sup>. Within different days reproducibility is limited by temperature control and not by pressure control. Measured densities of the mixtures are given in Tables 1, 2, and 3 as a function of temperature, pressure, and equilibrium pressure.

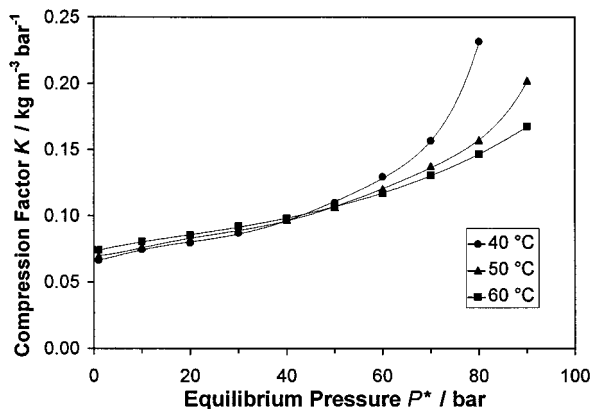
## Results

Densities of MM + CO<sub>2</sub> mixtures are shown in Figure 3 exemplarily at 40 °C. Points of measurement are connected to isobars by curve fitting in order to make related points visible. For constant equilibrium pressure, i.e., for constant composition, linear increase of the densities with system pressure is observed. We determined the critical pressure at 40 °C as 91 bar. Even beyond the critical point, the linear increase remains the same (Figure 4). The compression factor, that is, the slope of the linear increase, increases with the amount of CO<sub>2</sub>. At pressures below 40 bar, its value is almost independent of temperature. This is apparent in Figure 5. Figure 6 shows the densities of pure MM (straight lines) and of saturated MM (curved lines). At higher temperatures the density increase with pressure is less.

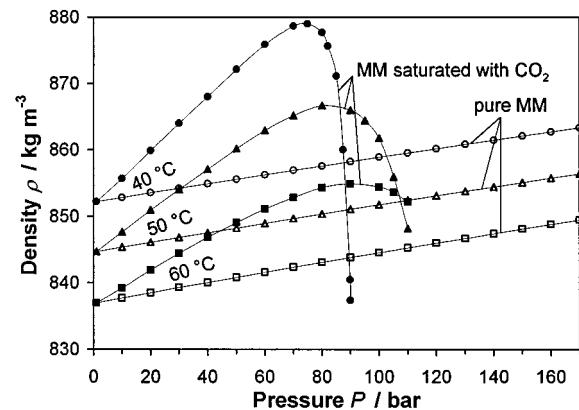
An identical equilibrium pressure at different temperatures means different compositions. Therefore the mea-



**Figure 4.** Isosteric (constant composition) densities of MM + CO<sub>2</sub> mixtures at 40 °C.



**Figure 5.** Increase of density with pressure at constant temperature and constant composition (compression factor).



**Figure 6.** Densities of pure MM and MM saturated with CO<sub>2</sub>.

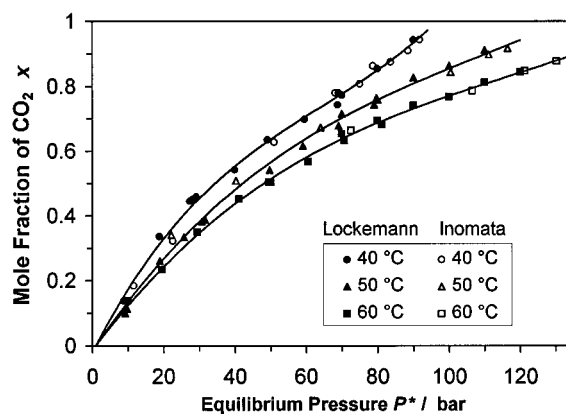
measurements are evaluated with equilibrium data of other authors. The equilibrium compositions of Inomata et al. (1989) and Lockemann (1994a,b) are expressed as mole fractions of CO<sub>2</sub>  $x$  with a third-order polynomial as a function of equilibrium pressure as

$$x = a_0 + a_1 \cdot (P^*/\text{bar}) + a_2 \cdot (P^*/\text{bar})^2 + a_3 \cdot (P^*/\text{bar})^3$$

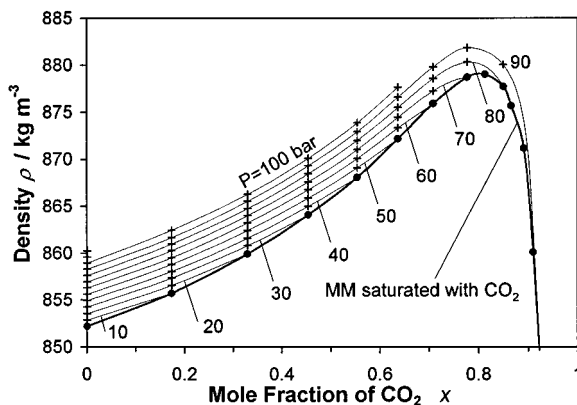
The coefficients at each temperature are given in Table 4. Figure 7 gives a comparison of equilibrium data and polynomials. Using this equation, the equilibrium pressures of the measurements are converted to mole fractions of carbon dioxide. Densities of  $(1-x)\text{MM} + x\text{CO}_2$  mixtures as a function of mole fraction are shown in Figure 8. Figure 9 shows that the compression factor is strongly dependent on composition but weakly dependent on temperature,

**Table 4.** Constants of Given Polynomial To Calculate Mole Fraction of CO<sub>2</sub> from the Equilibrium Pressure

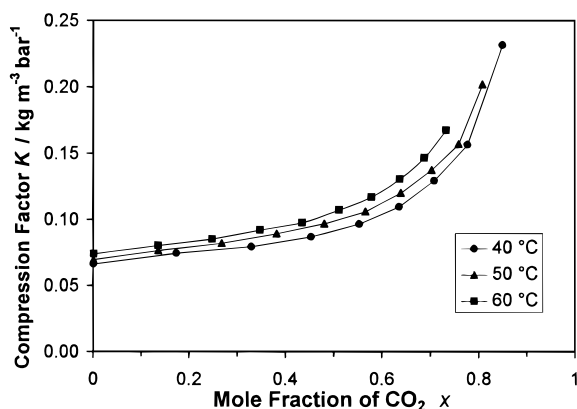
	40 °C	50 °C	60 °C
$a_3$	$1.185\,530 \times 10^{-6}$	$3.260\,320 \times 10^{-7}$	$2.714\,251 \times 10^{-7}$
$a_2$	$-2.292\,030 \times 10^{-4}$	$-1.075\,096 \times 10^{-4}$	$-9.510\,639 \times 10^{-5}$
$a_1$	$2.162\,870 \times 10^{-2}$	$1.618\,253 \times 10^{-2}$	$1.463\,275 \times 10^{-2}$
$a_0$	$-2.065\,260 \times 10^{-2}$	$-1.520\,479 \times 10^{-2}$	$-1.343\,224 \times 10^{-2}$



**Figure 7.** Polynomials of Table 4 to connect equilibrium pressure and composition obtained from equilibrium data for  $(1-x)\text{MM} + x\text{CO}_2$  mixtures of Lockemann (1994a,b) and Inomata et al. (1989).



**Figure 8.** Isobaric densities of  $(1-x)\text{MM} + x\text{CO}_2$  mixtures at 40 °C.

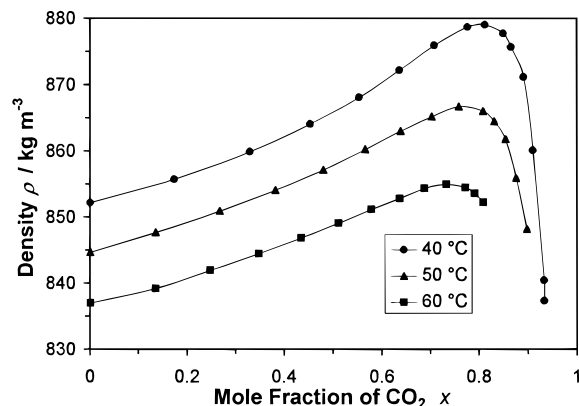


**Figure 9.** Compression factors of  $(1-x)\text{MM} + x\text{CO}_2$  mixtures.

whereas both composition and pressure have a significant influence on equilibrium density  $\rho^*$  (Figure 10). The equilibrium density increases with increasing amount of CO<sub>2</sub> despite the small density of CO<sub>2</sub> until it reaches a maximum between  $x = 0.75$  and  $x = 0.8$  depending on temperature. The small CO<sub>2</sub> molecules probably fill up

**Table 5.** Deviation at 40 °C,  $(\rho_{\text{calcd}} - \rho)/\text{kg m}^{-3}$ , of Calculated Densities from Measurements

pressure $P/\text{bar}$	equilibrium pressure $P^*/\text{bar}$ (molar load $\text{CO}_2 X^*$ )							
	1 (0.001)	10 (0.211)	20 (0.492)	30 (0.831)	40 (1.240)	50 (1.747)	60 (2.425)	70 (3.482)
1	-0.02							
10	-0.09	0.05						
20	-0.10	-0.09	-0.04					
30	-0.14	-0.13	-0.11	-0.02				
40	-0.16	-0.14	-0.13	-0.08	0.05			
50	-0.18	-0.16	-0.14	-0.09	0.02	-0.04		
60	-0.19	-0.17	-0.17	-0.07	0.03	-0.10	0.01	
70	-0.18	-0.19	-0.15	-0.07	0.05	-0.08	-0.05	0.00
80	-0.18	-0.18	-0.13	-0.06	0.07	-0.05	-0.07	-0.05
90	-0.18	-0.15	-0.09	-0.01	0.12	-0.01	-0.01	-0.02
100	-0.17	-0.19	-0.06	0.05	0.16	0.04		
110	-0.15							
120	-0.13							
130	-0.10							
140	-0.08							
150	-0.04							
160	0.00							
170	0.04							

**Figure 10.** Equilibrium densities of  $(1-x)\text{MM} + x\text{CO}_2$  mixtures.

gaps between the large MM molecules up to that maximum.

### Discussion

Vibrating-tube densimeters allow very precise and fast measurements, which can be used for the measurement of composition. To use the present results for this purpose, the density has to be expressed as a function of pressure, temperature, and composition. As Figure 4 suggests, the density can be expressed as a sum of equilibrium density and a pressure-dependent term, which is obtained from compression factor and departure from equilibrium pressure

$$\rho(P, T, X) = \rho^*(T, X) + K(T, X) \cdot [P - P^*(T, X)]$$

or simplified at constant temperature

$$\rho_T(P, X) = \rho_T^*(X) + K_T(X) \cdot [P - P_T^*(X)]$$

where  $X$  is the molar load (moles of MM per moles of  $\text{CO}_2$ ). Equilibrium density and compression factor can be described with polynomials, the equilibrium pressure results from the inverted polynomial of Table 4. The grade of the polynomials depends on the desired range and accuracy. For compositions greater than the composition at the maximum equilibrium density, the fitting becomes more difficult. The molar load  $X$  or mass load have proven to be an effective expression for composition, since they

require less coefficients than molar or mass fraction. The appendix gives exemplarily fitted coefficients for 40 °C, pressures from 1 to 170 bar, and equilibrium pressures from 1 to 70 bar to calculate densities deviating from measurements less than measurement accuracy (Table 5). An alternative description for density is also as

$$\rho_T(P, X) = \rho_T^*(X) \cdot \exp\{A_T(X) \cdot [P - P_T^*(X)]\}$$

with

$$A_T = b_0 \cdot \exp(b_1 \cdot X)$$

possible, where  $b_0$  and  $b_1$  are constants.

For densities below the equilibrium density a unique correlation between density and composition exists. For undersaturated mixtures with densities higher than equilibrium density (i.e., at pressures higher than the pressure at the maximum equilibrium density), further process information is needed to determine composition. We did not examine oversaturated mixtures in depth but found that a liquid phase at small oversaturation can exist for quite some time and the desorption of  $\text{CO}_2$  is very slow. We think that density measurement has proven to be a new method to rapidly determine online compositions at high pressures inside the two-phase envelope.

### Acknowledgment

We thank Johannes Stinner for performing experiments and Prof. Wagner for the IAPWS (International Association for the Properties of Water and Steam) program to calculate the water density. The measurements were performed from May to July 1996 and reported at the "GVC Fachausschussitzung Hochdruckverfahrenstechnik" in Hamburg in March 1997.

### Appendix

Equilibrium pressure from inverted polynomial of Table 4:

$$P_{40^\circ\text{C}}^*(x) = k - r/3$$

with  $a_0, a_1, a_2, a_3$  from Table 4 and

$$\begin{aligned}
 r &= a_2/a_3 & p &= (3s - r^2)/3 & m &= \sqrt{p/3} \\
 s &= a_1/a_3 & q &= 2r^3/27 - rs/3 + t & n &= \operatorname{arsinh}(q/2/m^3) \\
 t &= -x^*/a_3 + a_0/a_3 & & & k &= -2m \sinh(n/3)
 \end{aligned}$$

Compression factor:

$$K_{40^\circ\text{C}}(X) = b_0 + b_1X, \quad \text{with } b_0 = 6.652\,645 \times 10^{-2}, \\
 b_1 = 2.562\,025 \times 10^{-2}$$

Equilibrium density:

$$\rho_{40^\circ\text{C}}^*(X) = c_0 + c_1X + c_2X^2 + c_3X^3 + c_4X^4 + c_5X^5 + c_6X^6$$

with

$$\begin{aligned}
 c_0 &= 852.167\,5 & c_3 &= 2.015\,376 & c_6 &= -0.003\,634\,850 \\
 c_1 &= 18.309\,85 & c_4 &= -0.526\,08\,43 \\
 c_2 &= -6.200\,540 & c_5 &= 0.071\,667\,57
 \end{aligned}$$

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