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Shear Viscosity Coefficients of Compressed Gaseous and Liquid Carbon Dioxide at Temperatures Between 220 and 320 K and at Pressures to 30 MPa[1]

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The shear viscosity coefficients of compressed gaseous and liquid carbon dioxide have been measured with the torsional piezoelectric crystal method at temperatures between 220 and 320 K and at pressures to 30 MPa. The dependencies of the viscosity on pressure, density, and temperature and the dependencies of the fluidity (inverse viscosity) on molar volume and temperature have been examined. The measurements on the compressed liquid were correlated with a modified Hildebrand equation.

KEY WORDS: carbon dioxide; density; high pressure; viscosity.

1. INTRODUCTION

The thermophysical properties of carbon dioxide, and of mixtures containing carbon dioxide, are important for enhanced oil recovery and supercritical fluid separation processes. Carbon dioxide is also important for examining molecular structure–physical properties relationships because it has a large quadrupole moment but no dipole moment, which is a rather unusual combination.

Although the viscosities of compressed liquid carbon dioxide have been measured several times previously, the data are in poor agreement. It is expected that the data presented here will help to clarify the situation.

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2. APPARATUS AND PROCEDURES

The measurement method, apparatus, and procedures are essentially the same as have been reported for our work on argon [1] and methane [2]. The same piezoelectric quartz crystal of approximately 5-cm length and 0.5-cm diameter, discussed in Ref. 1, was used for the measurements on carbon dioxide. Viscosities, η, were derived from measured crystal resonance-curve bandwidths, Δf, using the equation

$$\eta = \frac{\pi f}{\rho}\left[\frac{M}{S}\right]^2 \cdot \left[\frac{\Delta f}{f} - \frac{\Delta f_{\text{vac}}}{f_{\text{vac}}}\right]^2 \tag{1}$$

where ρ is the fluid density, M is the crystal mass, S is the crystal surface area adjusted for thermal expansion and hydrostatic compression, and f is the resonant frequency of the crystal. The theory of the instrument is given in Ref. 3.

The measurements were made on commercially available, research-grade gases used without additional purification. The supplier claimed a purity of better than 99.99%. Chromatographic tests indicated less than 0.01% impurities.

Fluid densities were obtained from measured temperatures and pressures and a 32-term Benedict-Webb-Rubin equation of state [4]. The errors in the calculated densities are estimated to be smaller than 0.2%.

The measurement method and our apparatus have been validated previously, mainly by comparisons between our measurements on argon [1] and methane [2] and those of others using different methods. The estimated imprecision of our data for these fluids is smaller than 1% and the estimated experimental error is smaller than 2%. There is no published analysis of the estimated errors in the theory of the instrument. An examination of Eq. (1) indicates that errors in the viscosities of fluids for which there is an accurate equation of state are usually limited by the errors in the determination of Δf, which are estimated to be smaller than 1% in most cases.

Before beginning measurements on carbon dioxide, we measured the viscosities of compressed gaseous methane at 300 K. The data differed from our previous measurements [2] by less than 1%.

3. RESULTS AND DISCUSSION

3.1. Presentation of Data

The viscosities of compressed gaseous and liquid carbon dioxide, at eight temperatures between 220 and 320 K and at pressures to 20 MPa, are presented in Table I and Figs. 1 and 2. The viscosities of saturated liquid

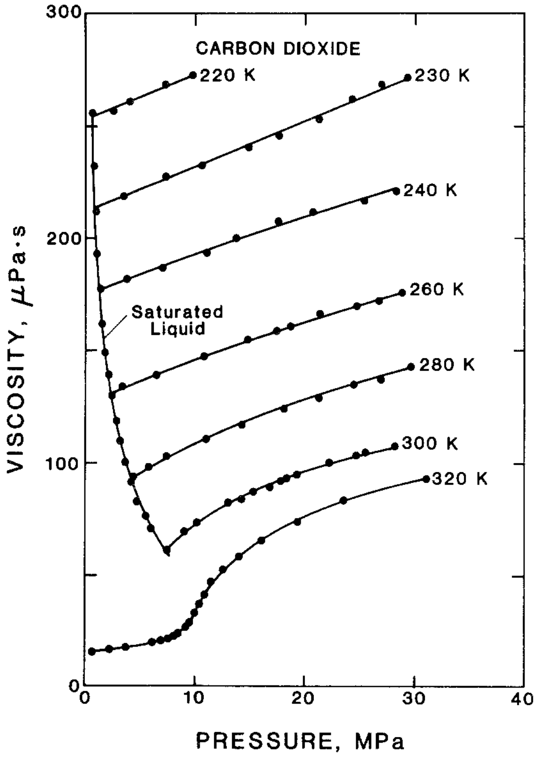

Fig. 1. Viscosities of compressed gaseous and liquid carbon dioxide as a function of pressure.

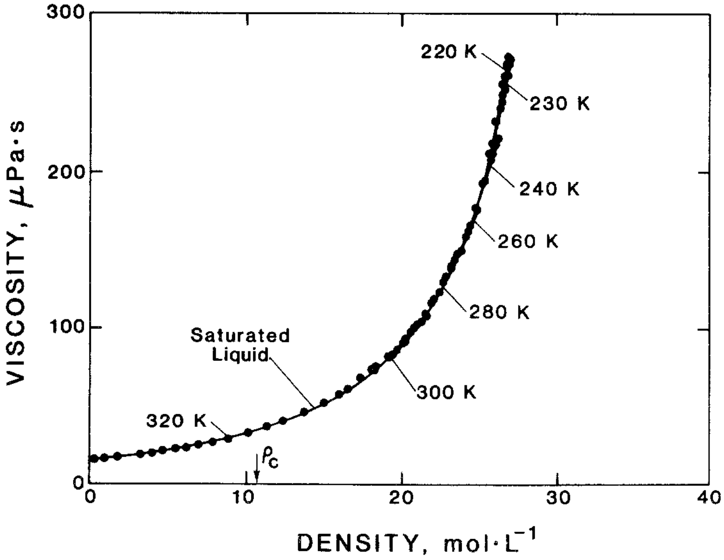

Fig. 2. Viscosities of compressed gaseous and liquid carbon dioxide as a function of density.

Table I. Viscosities of Compressed Gaseous and Liquid Carbon Dioxide

P (MPa)	ρ (mol $\cdot$ L^{-1})	η (μPa $\cdot$ s)
	$T = 320.00$ K	
31.0509	20.216	93.2
23.8247	19.082	82.7
19.3293	18.075	74.1
16.0370	17.006	65.7
13.9430	15.989	58.7
12.5309	14.947	52.9
11.5149	13.767	47.4
10.7546	12.346	41.4
10.3759	11.354	37.5
9.9798	10.116	33.4
9.5939	8.837	29.6
9.2632	7.827	27.2
8.9279	6.961	25.3
8.5397	6.146	23.7
8.1489	5.481	22.9
7.5531	4.666	21.5
6.9112	3.963	20.4
6.1260	3.258	19.4
3.8356	1.732	17.6
2.2622	0.938	16.8
0.7196	0.278	16.1
	$T = 300.00$ K	
28.1338	21.629	107.5
25.4675	21.329	104.6
24.6431	21.229	103.3
22.2594	20.922	100.5
19.2760	20.482	94.6
18.3004	20.322	92.7
17.7611	20.229	92.1
16.7726	20.049	88.5
15.2947	19.754	86.4
14.3100	19.537	83.5
13.0598	19.229	81.9
10.1685	18.300	73.6
7.3648	16.555	61.4
	$T = 280.00$ K	
29.6804	23.412	142.6
26.9814	23.203	137.5
24.5251	22.998	134.8
21.3094	22.708	129.5
18.1803	22.394	123.7
14.2561	21.941	117.2
11.0159	21.495	110.3
7.3825	20.868	102.8
5.8193	20.529	98.0
4.1540	20.091	93.2

Table I *(Continued)*

P (MPa)	ρ (mol · L^{-1})	η (μPa · s)
	$T = 260.00$ K	
28.9418	24.883	175.7
26.7123	24.749	172.4
24.7346	24.626	170.4
21.7006	24.428	165.9
18.6653	24.217	160.3
17.4183	24.126	158.8
14.8327	23.927	154.7
10.8377	23.591	147.4
6.4215	23.162	139.2
3.3852	22.819	133.7
2.4140	22.697	130.4
	$T = 240.00$ K	
28.3465	26.310	220.9
25.3016	26.165	217.5
20.7290	25.936	211.9
17.5745	25.768	207.5
13.6994	25.549	200.3
11.0203	25.388	194.1
6.9961	25.131	187.3
3.6984	24.902	182.4
	$T = 233.20$ K	
29.3554	26.834	259.2
24.0853	26.604	245.9
17.4583	26.290	234.9
12.3408	26.025	224.8
7.6370	25.761	215.8
1.6475	25.389	206.5
	$T = 230.00$ K	
29.3365	27.054	271.5
26.9187	26.954	268.8
24.5283	26.853	261.9
21.3391	26.713	253.4
17.6099	26.541	245.7
14.7080	26.401	240.7
10.7429	26.198	233.2
7.1939	26.006	228.2
3.3640	25.784	219.0
	$T = 220.00$ K	
9.7171	26.937	273.0
7.3673	26.829	269.0
3.9865	26.666	261.1
2.4998	26.592	257.4

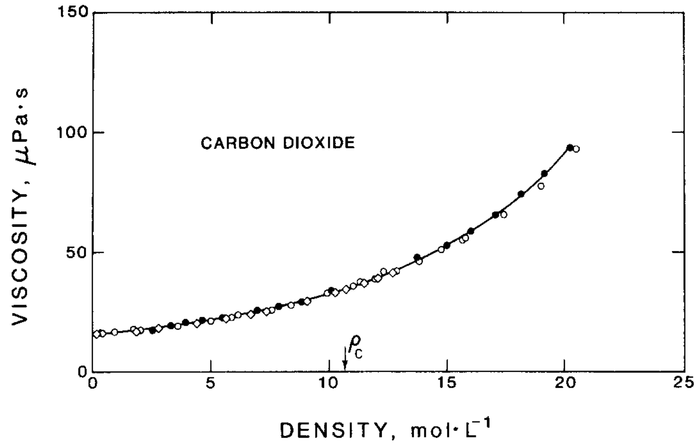

Fig. 3. Viscosities of compressed gaseous carbon dioxide at temperatures near 320 K: (●) this work, 320.00 K; (○) Michels et al. [5], 323.15 K; (◇) Iwasaki and Takahashi [6], 323.15 K.

carbon dioxide, at 14 temperatures between 220 and 285 K, are presented in Table II and Figs. 1–3. The dependencies of the viscosities on pressure, density, and temperature are similar to those of other fluids we have examined.

3.2. Comparisons with Other Data

The capillary tube measurements of Michels et al. [5] and the oscillating disk measurements of Iwasaki and Takahashi [6] are compared

Table II. Viscosities of Saturated Liquid Carbon Dioxide

T(K)	ρ (mol·L^{-1}) [9]	η (μPa·s)
220.00	26.499	256.0
225.00	26.070	232.6
230.00	25.656	211.8
235.00	25.183	193.1
240.00	24.754	177.8
245.00	24.247	162.1
250.00	23.781	149.3
255.00	23.239	139.4
260.00	22.710	129.6
265.00	22.122	118.8
270.00	21.504	110.1
275.00	20.831	100.6
280.00	20.091	91.7
285.00	19.271	83.0

with our measurements on compressed gaseous carbon dioxide at 320 K in Fig. 3. Although their measurements were made at a somewhat higher temperature than ours, the effect of the temperature difference on the viscosities is estimated to be less than 1% [6]. The differences between their data and ours are estimated to be smaller than 2% in this temperature range.

The torsional crystal measurements of Herreman et al. [7] and the capillary tube measurements of Ulybin and Makarushkin [8] are compared with our measurements on saturated liquid carbon dioxide in Fig. 4. The measurements of Herreman et al. differ from ours by less than 4%, except at the lower temperatures, where the differences increase to about 8%. The values of Ulybin and Makarushkin, which we estimated by extrapolating their compressed liquid data to the vapor pressure curve [9], differ from ours by about 3% at the higher temperatures, increasing to about 10% at the lower temperatures.

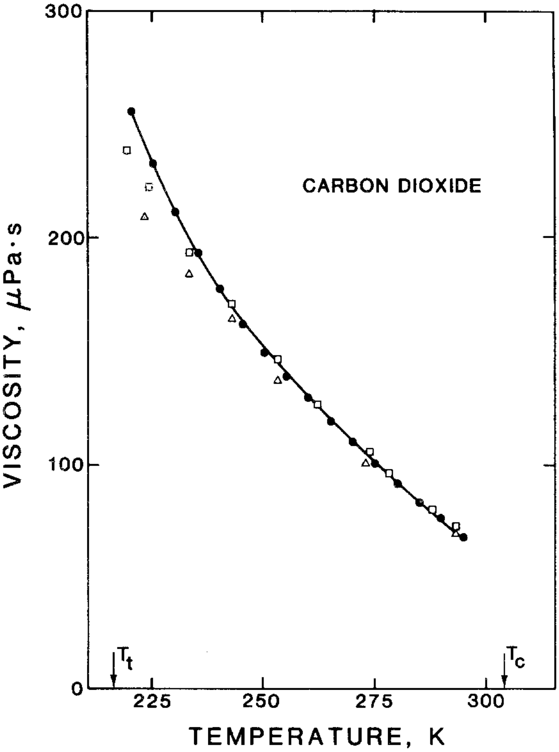

Fig. 4. Viscosities of saturated liquid carbon dioxide: (●) this work; [□) Herreman et al. [7]; (△) Ulybin and Makarushkin [8].

The torsional crystal measurements of Herreman et al. [7] and the capillary tube measurements of Ulybin and Makarushkin [8] are compared with our measurements on compressed liquid carbon dioxide at 233.2 K in Fig. 5. At low pressures the measurements of Herreman et al. differ from ours by less than 2%. However, their pressure dependence is somewhat smaller than ours. The pressure dependence obtained by Ulybin and Makarushkin looks quite similar to ours, but their viscosities differ systematically from ours by about 10% at this temperature.

3.3. Correlation of Fluidities of Compressed Liquid Carbon Dioxide

To our knowledge there are no published, global correlating equations for the viscosities of compressed gaseous and liquid carbon dioxide. Although Ulybin and Makarushkin [8] proposed an equation for $\Delta\eta$, the difference between the dense fluid viscosity and $\eta_0(T)$, the low-density gas value, an equation for $\eta_0(T)$ was not given.

We have examined our compressed liquid data using an equation proposed by Hildebrand [11]. Hildebrand has shown that the fluidities

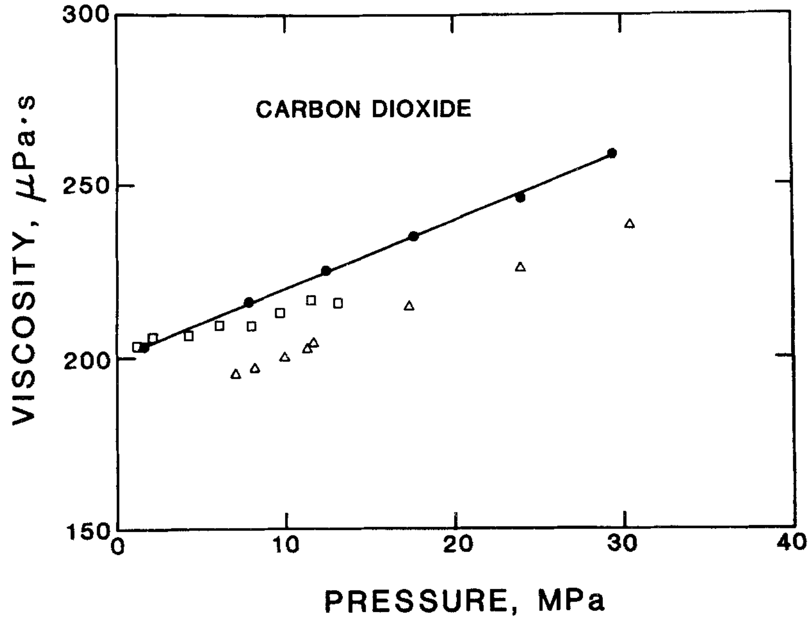

Fig. 5. Viscosities of compressed liquid carbon dioxide at temperatures near 233.15 K: (●) this work, 233.15 K; (□) Herreman et al. [7], 233.35 K; (△) Ulybin and Makarushkin [8], 233.15 K.

(viscosity^{-1})) of many liquids increase linearly with specific volume and can be described by the equation

$$\phi = \eta^{-1} = B(V - V_0) \tag{2}$$

where ϕ is the fluidity, V is the specific volume, V_0 is the estimated specific volume at zero fluidity, and B is an empirical coefficient, which is independent of temperature. The dependence of the fluidities of compressed liquid carbon dioxide on the molar volume is shown in Fig. 6. At small molar volumes the fluidities increase linearly with the volume at a fixed temperature, and there is clearly a small dependence on temperature at a fixed volume. Linear extrapolation of the compressed liquid isotherms to $\phi = 0$ gives $V_0 \cong 0.0295\ \mathrm{L \cdot mol^{-1}}$, and the temperature dependence of B can be described by

$$B(T) = 0.537 - \exp(6.726 - 0.0433 \times T) \tag{3}$$

A comparison of our highest-density data ($>22.0\ \mathrm{mol \cdot L^{-1}}$) with Eqs. (2) and (3) is shown in Fig. 7. The measured and calculated viscosities differ by less than 2%. Figure 7 also shows the data of Herreman et al. and of

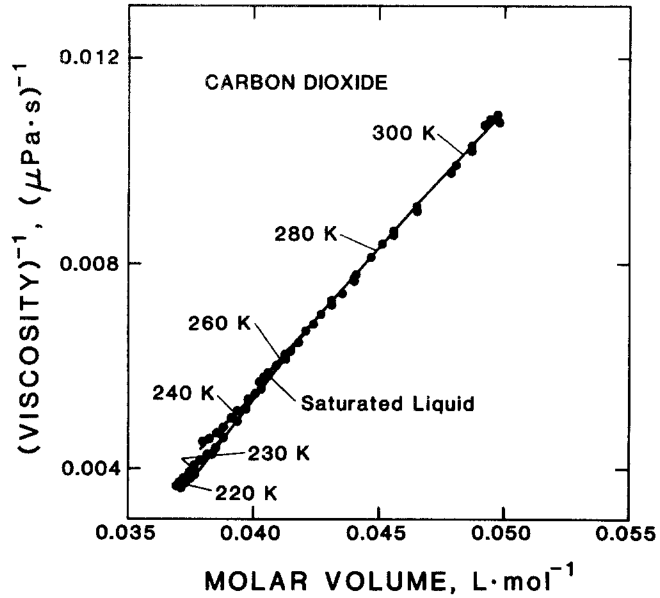

Fig. 6. Fluidities (viscosity^{-1}) of compressed liquid carbon dioxide as a function of molar volume.

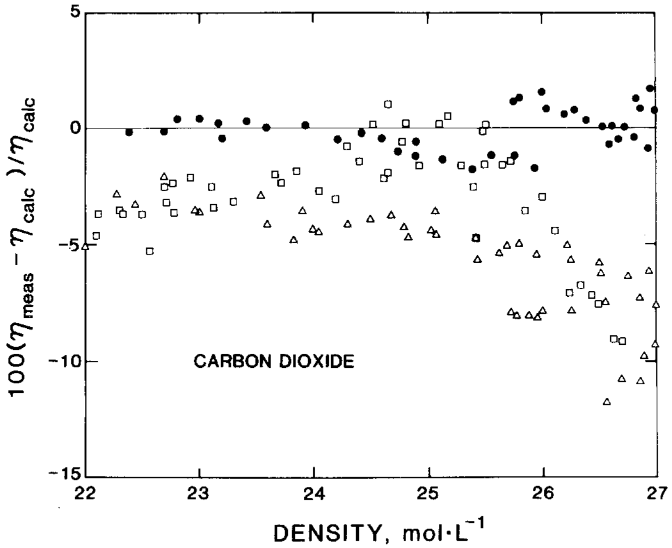

Fig. 7. Differences between measured viscosities of compressed liquid carbon dioxide and Eqs. (2) and (3): (●) this work; (□) Herreman et al. [7]; (△) Ulybin and Makarushkin [8].

Ulybin and Makarushkin in this density range. Their data differ from ours by about 4% at the lower densities and about 10% at the higher densities, as mentioned previously.

4. ERROR ESTIMATE

Based on the performance of the apparatus on other fluids, on an examination of the components of the error in the data reduction equation, and on the internal consistency, as shown by differences from a correlating equation, we estimate that the experimental error of our measurements on carbon dioxide is smaller than 2%.

5. SUMMARY

New absolute measurements of the shear viscosity coefficients of compressed gasous and liquid carbon dioxide are reported. Our experimental error is estimated to be smaller than 2%. Our measurements on compressed gaseous carbon dioxide differ from previous work by less than the combined estimated errors. Our measurements on compressed liquid carbon dioxide at the lower densities differ from previous work by approximately the combined errors. The differences increase with density, however, to about 8–10% at the highest densities. Our measurements on the compressed liquid have been correlated using a modified Hildebrand equation.

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