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The Viscosity of Liquid Carbon Dioxide

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The paper reports new masurements of the viscosity of liquid carbon dioxide along three isotherms at 260, 280, and 300 K for pressures up to 100 MPa. The measurements have been carried out in a vibrating-wire viscometer and have an estimated accuracy of ±0.5%. The results are employed to distinguish between conflicting data sets that already exist in the literature and that have inhibited accurate representations of the viscosity of this important fluid. It is shown that the experimental results can be represented with a high precision by means of procedures founded on the hard-sphere theory of liquids, although the observed density dependence of the viscosity is different from that characteristic of hydrocarbons.

KEY WORDS: carbon dioxide; hard-sphere theory; liquid viscosity.

1. INTRODUCTION

In 1990 the results of a review of the transport properties of carbon dioxide were reported [1]. In particular, the review contained an examination of the viscosity of carbon dioxide over the complete range of thermodynamic states from $200\,\mathrm{K} \leqslant T < 1500\,\mathrm{K}$ for pressures up to 100 MPa including both gaseous and liquid phases. In the liquid phase, four extensive sets of measurements were revealed: the first by Golubev et al. [2–4], with a capillary viscometer with a claimed accuracy of 2%; the second by Ulybin and Makarushkin [5–7], with the same type of instrument but an accuracy

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of ±1.7%; the third by Diller and Ball [8], with an oscillating quartz-crystal viscometer with a claimed accuracy of ±2%; and a final set due to Herreman et al. [9]. The analysis revealed discrepancies between the various authors of as much as 20% at low temperatures. However, there was no theoretical or other guidance to permit a selection of one set of data over another.

Prompted by these findings, van der Gulik et al. [10] undertook a series of careful measurements with a vibrating-wire viscometer of the viscosity of liquid carbon dioxide along an isotherm at 300.01 K. However, the measurements at this temperature failed to provide a discriminant among the previous sets of results. For this reason, the final representation reported by Vesovic et al. [1] had an uncertainty of as much as 5% in the liquid-phase viscosity. It was felt that this disappointing result for such a simple commonplace and important fluid should encourage further measurements.

The present paper describes the results of new measurements of the viscosity of liquid carbon dioxide in the temperature range 260 to 300 K at pressures up to 100 MPa. The results are intended to supplement the existing measurements which extend to lower temperature and, by virtue of their superior accuracy, identify which of the earlier sets of measurements are in error.

2. EXPERIMENTS

The measurements of the viscosity of liquid carbon dioxide were performed in a vibrating-wire viscometer described in detail elsewhere [11]. The instrument was employed unchanged for the present measurements, except for the fact that the pressure vessel containing the viscometer cell was immersed in a bath allowing temperatures as low as 200 K to be achieved. The sample of carbon dioxide employed was supplied by the British Oxygen Company with a stated purity of better than 99.995%. As described in our earlier work [11], the viscometer was calibrated with respect to the viscosity data of toluene, *n*-hexane, *n*-heptane, *n*-octane, and *n*-decane reported by Gonçalves et al. [12] and Knapstad et al. [13] under saturation conditions near room temperature. The calibration was employed to determine the radius of the vibrating wire and the density of the tungsten material used to form it. The values were entirely consistent with those obtained earlier [11].

In order to evaluate the viscosity of the fluid from masurements of the characteristics of the damped oscillations of the vibrating wire, it is necessary to make use of the density of the fluid. For carbon dioxide we have made use of the equation of state of Ely et al. [14, 15]. Accounting for the precision of the measurements, the uncertainty in the density of the fluid and the estimated uncertainty in the viscosity data employed for calibration, the overall accuracy of the viscosity data reported here is estimated to be one of ±0.5%.

3. RESULTS

The experimental results for the viscosity of carbon dioxide are listed in Table I along three isotherms, at 300.00, 280.02, and 260.04 K, for

Table I. Viscosity of Liquid Carbon Dioxide

Temperature (K)	Pressure p (MPa)	Density ρ (kg·m^{-3})	Viscosity η (mPa·s)
260.04	5.95	1016.2	0.1310
	12.70	1045.4	0.1445
	12.80	1045.8	0.1451
	19.69	1069.3	0.1552
	19.75	1069.6	0.1554
	29.17	1096.0	0.1697
	45.24	1132.2	0.1924
	45.36	1132.3	0.1921
	59.83	1158.4	0.2130
	60.07	1158.9	0.2117
	80.94	1189.5	0.2399
	81.32	1189.9	0.2402
280.02	6.33	907.4	0.0961
	6.34	907.3	0.0960
	13.77	962.1	0.1124
	13.84	962.5	0.1124
	22.46	1003.9	0.1278
	23.06	1006.2	0.1284
	23.14	1006.4	0.1278
	32.98	1040.9	0.1424
	32.99	1040.8	0.1423
	44.77	1073.4	0.1576
	44.90	1073.7	0.1578
	53.39	1093.2	0.1685
	56.38	1099.6	0.1711
	56.56	1099.9	0.1714
	68.45	1122.9	0.1851
	68.73	1123.4	0.1855
	68.74	1123.4	0.1857
	72.90	1130.6	0.1998
	80.38	1142.9	0.1981
	80.62	1143.2	0.1987
	90.70	1158.3	0.2104
	90.83	1158.6	0.2099
	99.82	1170.9	0.2191
	100.00	1171.1	0.2204

Table I. *(Continued)*

Temperature (K)	Pressure p (Pa)	Density ρ (kg · m^{-3})	Viscosity η (mPa · s)
300.00	7.53	735.6	0.0633
	7.54	735.8	0.0633
	8.01	753.8	0.0658
	8.01	753.8	0.0657
	11.63	828.1	0.0791
	11.64	828.2	0.0791
	16.65	881.2	0.0911
	16.67	881.3	0.0909
	25.68	939.6	0.1068
	25.70	939.7	0.1068
	34.73	979.8	0.1201
	34.76	979.9	0.1203
	43.04	1008.8	0.1299
	43.07	1008.9	0.1304
	50.66	1031.2	0.1391
	50.69	1031.3	0.1395
	58.43	1051.1	0.1475
	58.50	1051.3	0.1474
	65.52	1067.4	0.1551
	65.58	1067.5	0.1551
	71.24	1079.4	0.1606
	71.34	1079.6	0.1603
	79.20	1094.8	0.1685
	86.28	1107.4	0.1751
	86.39	1107.6	0.1754
	93.20	1118.9	0.1821
	93.42	1119.3	0.1822
	99.30	1128.5	0.1880
	99.57	1128.9	0.1880

pressures up to 100 MPa. Measurements were also attempted at lower temperatures but failed to yield satisfactory results since the viscosity of the fluid appeared to be time dependent. In order not to interrupt the presentation of the main results, a discussion of this phenomenon is postponed until Section 6.

For the purposes of comparison, the experimental viscosity data have been represented as a function of density by means of a formulation based upon the hard-sphere theory of liquid transport [16]. We define a reduced, experimental viscosity, η^*, by means of the equation

$$\eta^* = 6.035 V^{2/3} \eta / (MRT)^{1/2} \tag{1}$$

in which η is the viscosity of the fluid, V its molar volume, T the temperature, M the molar mass, and R the universal gas constant. All

Table II. Coefficients a_i of Eq. (2) for the Representation of the Viscosity of Liquid Carbon Dioxide

i	a_i
0	12.6634
1	−38.4173
2	56.9902
3	−40.5114
4	11.1237

quantities in Eq. (1) are measured in SI units. The experimental values of η^* have then been represented by the equation

$$\ln(\eta^*) = \sum_{i=0}^{4} a_i [\ln V/V_0]^i \tag{2}$$

which has been found to be a suitable form for normal hydrocarbons and several other liquids [16]. The coefficients of Eq. (2) are collected in Table II, together with the values of V_0 at each temperature in Table III. Figure 1 presents a plot of the deviations of the present experimental data from this representation, which reveals that the maximum deviation is no more than ±0.6% while the standard deviation is one of ±0.3%, which is commensurate with the estimated precision of the measurements.

The same representation permits a comparison of the present experimental data in the temperature range of interest with the results of earlier work which is contained in Figs. 2 and 3. In Fig. 2 the deviations of the earlier results from the present correlation are plotted as a function of temperature, whereas in Fig. 3 they are plotted as a function of density. Considering first Fig. 2 it can be seen that below a temperature of 293 K, the experimental data of Golubev et al. [2–4] deviate from the present results by between 2 and 3% at most densities, which is consistent with the estimated mutual uncertainty of about 2.5%. However, Fig. 3 reveals that

Table III. Characteristic Molar Volumes for Carbon Dioxide

T (K)	$10^6 V_0$ ($m^3 \cdot mol^{-1}$)	$10^6 V_0^a$ ($m^3 \cdot mol^{-1}$)
260.04	20.204	20.216
280.02	19.936	19.916
300.00	19.695	19.660

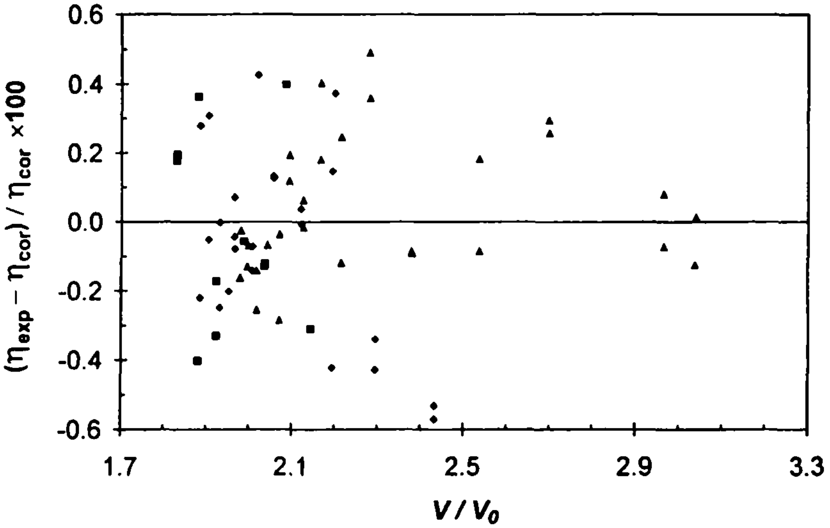

Fig. 1. Deviations of the present results for the viscosity of liquid carbon dioxide from the correlation of them by Eq. (2): (■) 260.04 K; (◆) 280.02 K; (▲) 300.00 K.

at the highest densities, the results of Golubev et al. [2–4] differ substantially from each other and that the earliest set [2] are in much better agreement with the present results. The data of Ulybin and Makarushkin [5–7] are also consistent with the present results for temperatures below 293 K, but at higher temperatures and lower densities the departure amounts to as much as −10%. At the lower temperatures the results of Diller and Ball [8] are systematically above those of all other workers including the present data and reveal a completely different density dependence. On the other hand, their results at 300 K are in very good agreement with those of the present work. The results of van der Gulik et al. [10] at 300 K reveal a density dependence in Fig. 2 which is essentially identical to that reported here except at the lowest pressures. Generally, the data of van der Gulik et al. lie only 2–3% below the present data, which is an amount consistent with the estimated mutual uncertainty.

On the basis of this analysis we conclude that most of the earlier measurements of the viscosity of liquid carbon dioxide are burdened with a systematic uncertainty and that only the earliest measurements of Golubev [2] and those of Ulybin and Makarushkin [5–7] for temperatures below 293 K should be included in any future critical evaluation of the viscosity of this liquid. Such an evaluation is not attempted here since further measurements at lower temperatures are known to be in progress [17].

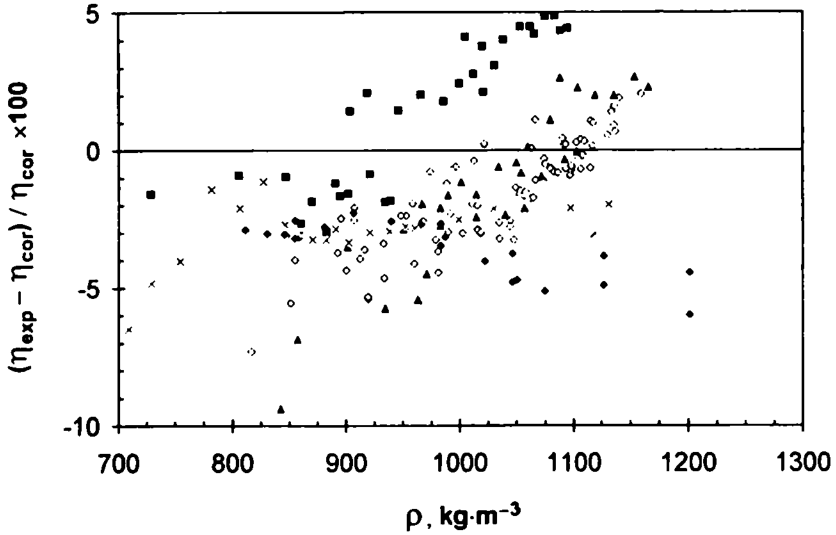

Fig. 2. Deviations of earlier exprimental data for the viscosity of liquid carbon dioxide from the representation of the present results as a function of density: ◇ [2]; ◆ [3, 4]; ▲ [5–7]; ■ [8]; × [10].

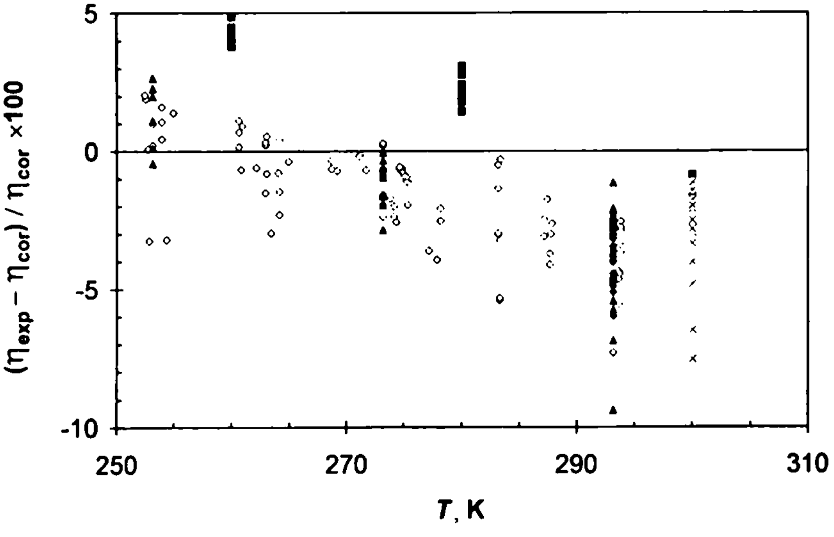

Fig. 3. Deviations of earlier experimental data for the viscosity of liquid carbon dioxide from the representation of the present results as a function of temperature: ◇ [2]; ◆ [3, 4]; ▲ [5–7]; ■ [8]; × [10].

4. THE HARD-SPHERE THEORY

The fact that Eq. (1) provides a successful means of representing the present experimental data confirms the usefulness of the hard-sphere theory of liquid transport upon which it is based [16, 18]. This theory for smooth hard spheres demonstrates that the viscosity of a fluid is a funtion only of the molar volume of the fluid divided by a characteristic molar volume V_0, depending upon the diameter of the spherical molecules. For real fluids composed of spherical molecules, the value of V_0 is expected to depend upon temperature, reflecting the influence of the finite steepness of the repulsive wall of the intermolecular potential. For nonspherical molecules, it is more appropriate to employ the rough hard-sphere theory [16]. This retains all of the essential features of the smooth hard-sphere theory but account of the shape of the molecules is taken in a factor R_η which is a characteristic of the molecular system alone, so that the rough hard-sphere viscosity η^*_{RHS} is related to that of the smooth hard sphere η^*_{SHS} by the equation

$$\eta^*_{\mathrm{RHS}} = R_\eta \eta^*_{\mathrm{SHS}} \tag{3}$$

These facts have been exploited by Assael et al. [16] to develop a predictive scheme for the viscosity of liquid hydrocarbons. It is therefore interesting to assess how well this procedure is able to represent the experimental viscosity data for carbon dioxide.

Assael et al. [16] have represented the reduced viscosity of real liquids by means of the equation

$$\log(\eta^*/R_\eta) = \sum_{i=0}^{7} b_{\eta i}(V_0^{\mathrm{u}}/V)^i \tag{4}$$

and have determined the optimum values of R_η, $b_{\eta i}$, and V_0^{u} for a number of liquids. Using their function, the values of R_η and V_0^{u} along each isotherm that best represent the present viscosity data for carbon dioxide have been determined.

The appropriate value of R_η has been found to be 0.9925, while the optimum values of V_0^{u} are included in Table III. Naturally, the values of V_0^{u} for this universal correlation differ slightly from those required by the special representation of Eq. (2). Figure 4 contains a plot of the deviations of the present experimental data for the viscosity of carbon dioxide from their representation by means of the universal correlation of Eq. (4). It is clear that the deviations are rather larger than from the optimised function of Eq. (2) and reveal that the function η^*/R_η for carbon dioxide is significantly different from that for hydrocarbons. However, it is perhaps worth noting that given the scheme of Assael et al. [16] includes molecules

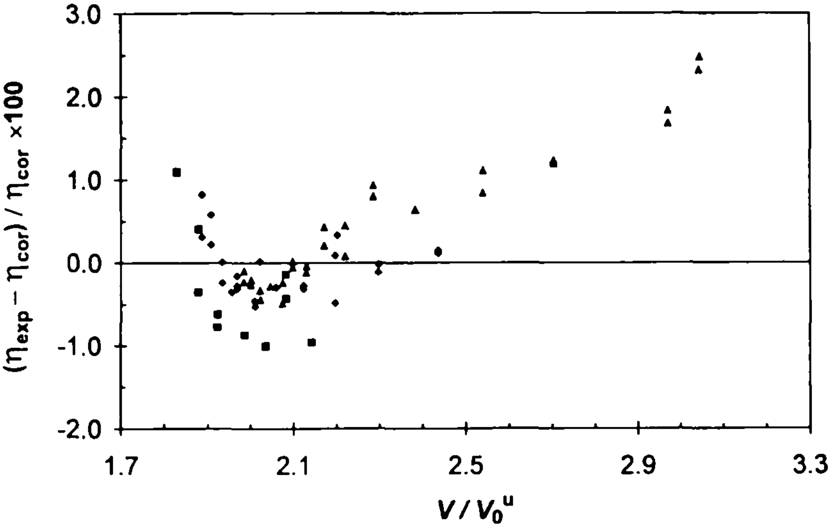

Fig. 4. Deviations of the present viscosity data for liquid carbon dioxide from the universal correlation of Assael et al. [16]: (■) 260.04 K; (◆) 280.02 K; (▲) 300.00 K.

such as tetradecane, it is remarkable that the density dependence of the viscosity of liquid carbon dioxide should be as similar as it is.

5. CONCLUSIONS

New measurements of the viscosity of liquid carbon dioxide have identified, unequivocally, systematic uncertainties in some earlier experimental data. At the same time, other experimental data, extending over a wide range of temperature, have been confirmed. This should permit a much improved representation of the viscosity of carbon dioxide over the entire range of fluid states to be formulated once other, more extensive, measurements have been concluded.

6. POSTSCRIPT

It is felt worthwhile to record here an observation made during the course of these measurements. Below a temperature of 260 K it was observed that the "apparent" viscosity of the liquid carbon dioxide increased with time on a time scale of hours. The increase was so great that at the highest pressures, the change reached a factor of three in the viscosity without any observable concomitant change in the fluid density. Once the increase had occurred, it was not possible to reduce the apparent viscosity by reducing the pressure even on a time scale of days. It was, however, possible to reduce the apparent viscosity slightly by heating the vibrating wire electrically. If the temperature of the liquid was returned to 300 K, the viscosity of the fluid obtained previously at that temperature was recovered within experimental error. At the temperatures and pressures of the present study the state of the liquid is far removed from the melting line [19] so that there is no possibility of a bulk phase transition. These observations are similar to those reported by van der Gulik [17] with a similar instrument but in the gas phase of carbon dioxide.

Attempts were made to establish the cause of this phenomenon by observing the vibrating wire directly with a microscope. There was no sign of any phase change in the liquid phase near to the wire which would have indicated a solid layer formed on the wire. Such a layer would increase the effective diameter of the wire and thus increase the damping in the wire and so the apparent viscosity. The reasons for this behavior thus remain obscure, but given that it has been observed in both gaseous and liquid phases with carbon dioxide in the presence of a fine tungsten wire, it is probably worthy of further investigation.

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