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The Viscosity of Liquid Carbon Dioxide[1]

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The viscosity coefficient of carbon dioxide in the liquid phase has been measured by means of a vibrating-wire viscometer at temperatures of 220, 230, 240, 260, and 280 K. The measurements extended beyond both phase transition lines into the coexistence region (superheated liquid) and into the solid range (undercooled liquid). At 280 K, the measurements extended only to 350 MPa since no density data are available for high pressures. The accuracy of the measurements is estimated to be 1%. The agreement with the data of Ulybin and Makarushkin is rather good, but our values are in general a few percent lower than those of Diller and Ball. The results show, for the most part, a linear pressure dependence for the various isotherms, with a common intersection with the negative pressure axis of 113.7 MPa. The fluidity, the reciprocal of the viscosity, shows a linear dependence of the molar volume in adjacent density ranges. After reduction of the molar volume with the volumes of close packing, two sets of linear functions result, with common intersections of the axis for $V/V_0 = 1.31$ and $V/V_0 = 1.40$.

KEY WORDS: carbon dioxide; high pressure; low temperature; liquid; viscosity coefficient.

1. INTRODUCTION

In his article "On the Theory of the Friction of Liquids" [1], van der Waals Jr. stated that the explanation for the viscosity of gases, *viz.*, that molecules diffusing from one gas layer to another at the same time transport momentum from one layer to another, cannot be true for the viscosity of liquids, since the viscosity of gases increases with temperature, while that of liquids decreases. He proposed that the forces that the molecules exert on each other on impact might furnish the explanation of viscosity.

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Brillouin [2] was also of opinion that the idea of a mean free path has to be abandoned for liquids, since the molecules are continuously in a state of collision with all their neighbors. Andrade [3], in his turn, considered the molecules in a liquid as particles vibrating in a stationary position, forming a temporary union at the periphery of molecules in adjacent layers.

So the classical picture for the viscosity of liquids is that of molecules bouncing around in cages formed by their neighbors, whereby momentum is exchanged during collisions. The viscosity coefficient is then determined by the number of collisions per unit of time and volume and by the efficiency of the exchange. On the other hand, according to the idea of Bernoulli, the pressure is determined by the change of momentum during collisions of the molecules and is, therefore, also proportional to the number of collisions. This pressure is, according to van der Waals Sr. [4], not the pressure which we measure but the pressure which the molecules experience, i.e., the combination of the measured pressure and the internal pressure due to the intermolecular forces. The latter is generally considered to be a constant background force keeping the molecules together. In this view we may assume that the magnitude of the momentum mv is dependent only on temperature, in which case the pressure along an isotherm is proportional to the number of collisions only, as is also the case for the viscosity coefficient. Therefore, the viscosity coefficient may be expected to be proportional to the pressure, and that is exactly what we have found in this investigation. Even the isotherms show a common intersection with the negative pressure axis of 113.7 MPa, and that points to a constant, temperature-independent internal pressure.

The fluidity, the reciprocal of the viscosity coefficient, is found to be a linear function of the molar volume in adjacent density ranges. Comparison of the experimental values with the results of computer simulations on hard spheres allows us to determine values for the volumes of close packing. When the molar volumes are reduced with these slightly temperature-dependent values of the volumes of close packing, we again obtain linear functions with common intersections of the axis. From this phenomenon we may conclude that the number of collisions is inversely proportional to the free volume $V - V_B$, where V_B is the value of the intersection with the volume axis and is interpreted as being an excluded volume.

Combining these two types of linear relation, we obtain a simple equation of state for an isotherm, namely, $(p + p_i)(V - V_B) = \text{Const}$, where p_i is the value of the intersection with the pressure axis. This equation is reminiscent of the van der Waals equation of state, which is valid for low densities. This resemblance encourages us to interpret p_i as the internal pressure and V_B as the excluded volume, but we would like to stress here that this equation is valid only within the precision of the present measurements. Moreover, in different temperature and density ranges different values for p_i and V_B are found.

The efficiency of the exchange of momentum during a collision is clearly temperature dependent according to our measurements. With a constant background force, the momentum mv may be supposed to be proportional to the square root of the temperature, since the velocity can be related to the kinetic energy $mv^2/2 = (3/2)kT$. In that case a fourfold temperature increase would cause a doubling of the momentum and therefore a halving of the number of collisions to obtain the same pressure and, so, a halving of the viscosity coefficient at that pressure. However, even with this correction the efficiency of the momentum exchange of a collision at 220 K is about two times larger than that of a collision at 300 K.

2. METHOD AND RESULTS

The viscosity coefficient of carbon dioxide in the liquid phase was measured by means of a vibrating-wire viscometer suited for pressures up to 1 GPa with the use of the free damped oscillation method [5, 6]. The measurements were performed at temperatures of 220, 230, 240, 260, and 280 K, and extended beyond both phase transition lines into the coexistence region (superheated liquid) and into the solid range (undercooled liquid). At 280 K the measurements extended only to 350 MPa since no density data are available for high pressures. The measurements in the metastable states had, as a matter of course, to be performed rather quickly, and therefore, the accuracy of the measurements is somewhat lower than usual: It is estimated to be 1%. For the calculation of the density from the temperature and pressure, the equation of state of Ely et al. [7] was applied. The details of the method, lists of the 169 data points, and the table of equation coefficients would require too much space here and will be reported soon in a more extensive article.

The experimental results for the viscosity coefficient are shown in Fig. 1 as a function of the density. The filled circles represent our newly obtained results in the stable liquid range along the various isotherms; the open circles, those measured in the metastable undercooled liquid state beyond the liquid–solid phase transition line. The measurements in the metastable superheated liquid state beyond the liquid–vapor phase transition line nearly coincide with those measured in the stable state and therefore cannot be distinguished on this scale. The crosses represent already published results [8] of the viscosity of liquid carbon dioxide at three temperatures near the critical temperature, i.e., 300, 303, and 308 K, and at pressures from 8 up to 450 MPa. Literature data of Diller and Ball

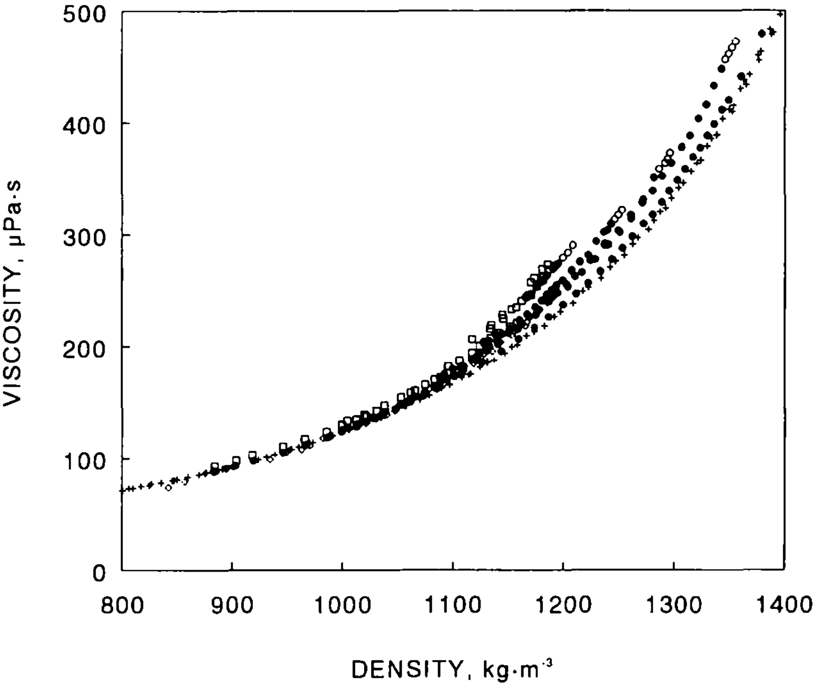

Fig. 1. The viscosity coefficient of carbon dioxide as a function of density at temperatures of 220, 230, 240, 260, and 280 K: (●) in the stable state; (○) in the metastable state; (+) earlier reported data [8]; (□) Diller and Ball [9]; (◇) Ulybin and Makarushkin [10].

[9] are given as open squares, and data of Ulybin and Makarushkin [10] as open diamonds.

Figure 2 presents, in particular, the linear pressure dependence of the various isotherms with the common intersection with the negative pressure axis at 113.7 MPa, which is interpreted as the internal pressure p_i. As can be seen, the linearity holds for the entire liquid isotherms at temperatures near the triple-point temperature (216.58 K), i.e., at 220, 230, and 240 K, and for the middle part of the isotherms taken at higher temperatures up to the critical temperature (304 K). According to our measurements on methane [11, 12] at higher pressures, the molecules come so near to each other that the attractive force decreases and thus also the internal pressure decreases. Here, not enough high-pressure data could be obtained, and due to a lack of density data, the data measured are too uncertain to draw such conclusions, but the tendency to bend upward is clearly seen. Near the critical point the results begin to show vapor character.

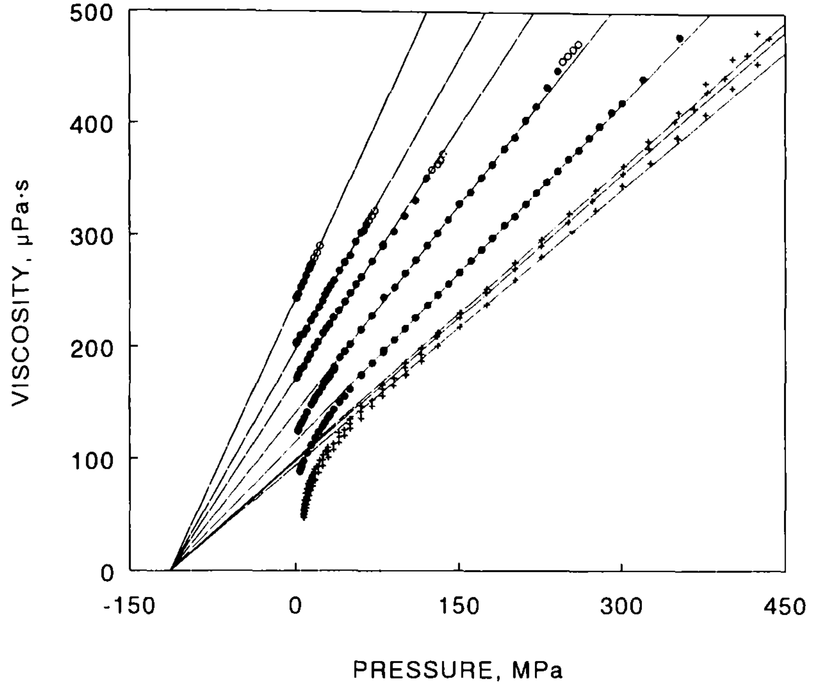

Fig. 2. The viscosity coefficient of carbon dioxide as a function of pressure at temperatures of 220, 230, 240, 260, and 280 K: (●) in the stable state; (○) in the metastable state; (+) earlier reported data [8].

As mentioned in our earlier paper [8], comparison of the experimental results with the MD results for hard spheres, using an effective volume of close packing as an adjustable parameter, led to the conclusion that, due to the elongated shape of carbon dioxide molecules, a form factor of 0.881 had to be introduced. In the present analysis we have multiplied the MD results [13] with this form factor and fitted both the present and the former experimental results to the resulting curve. For the present data, this procedure leads to a satisfying fit and acceptable values for the volumes of close packing V_0; for our earlier data, slightly lower values for V_0 were obtained than reported in Ref. 8.

Figures 3 and 4 show the linear molar volume dependence of the fluidity, i.e., the reciprocal of the viscosity. The molar volume has been reduced with the volumes of close packing for the various temperatures, obtained in the manner described in the preceding paragraph. This procedure resulted in two sets of linear functions with, again, common intersections of the axis. The first set, with intersection value $V/V_0 = 1.31$, holds for the entire liquid isotherms at 220, 230, and 240 K and for the high-pressure part of the isotherms taken at 260, 280, 300, 303, and 308 K. For the low-pressure part of the latter isotherms, different linear functions are observed, with a common axis intersection at $V/V_0 = 1.40$. Figure 3 shows the high-density low-molar volume data and, in particular, the transition from one set to the other at $V/V_0 = 1.80$. In the view outlined above, this means a transition from a small excluded volume $1.31V_0$ to a larger excluded volume $1.40V_0$ with increasing molar volume. Figure 4 shows the total extension of the linearity, which ends at $V/V_0 = 2.92$ for the data taken near the critical point. The various ranges are named in accordance with our earlier papers.

This representation offers the opportunity to calculate the deviations of the data from these linear functions in a simple way; the results are shown in Fig. 5. In contrast with our earlier paper, where three ranges were distinguished, two of which were nearly identical, for simplicity we prefer here to distinguish two ranges for our previous data [8]. Figure 5 shows,

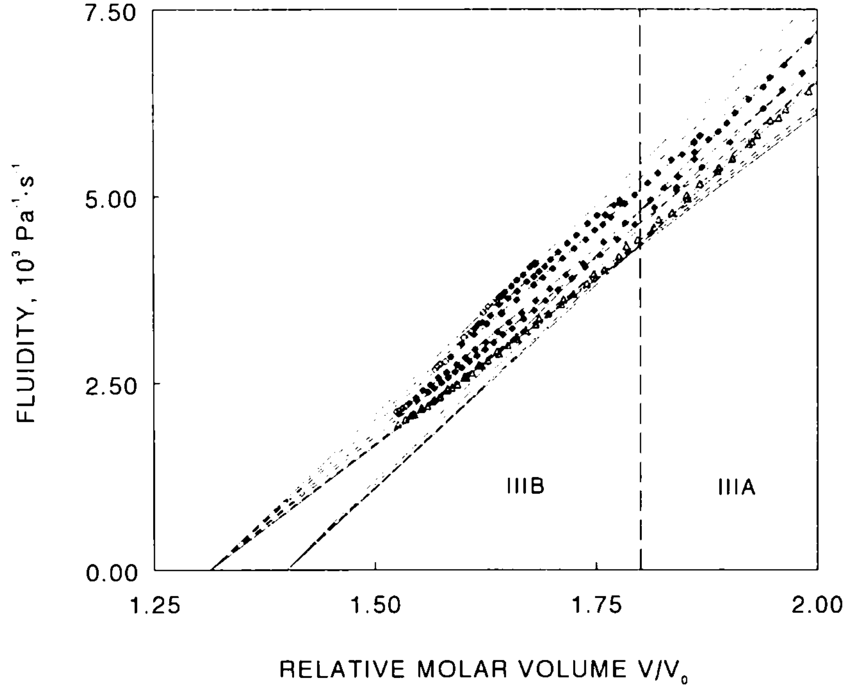

Fig. 3. The fluidity, the reciprocal of the viscosity coefficient, of carbon dioxide as a function of the reduced molar volume for high densities: (◆) in the stable state; (·) in the metastable state; (△) earlier reported data [8].

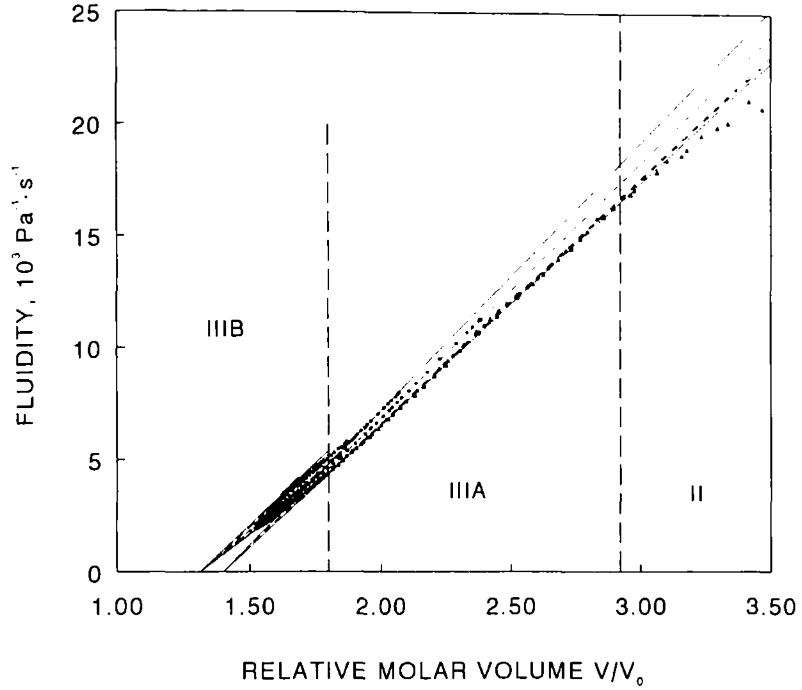

Fig. 4. Extended plot of the fluidity, the reciprocal of the viscosity coefficient, of carbon dioxide as a function of the reduced molar volume: (◆) in the stable state; ( ) in the metastable state; (△) earlier reported data [8].

however, that there are also arguments for the other possibility. Which choice is correct depends on (as yet unavailable) data at higher temperatures. The question is interesting, since a third range signifies the transition to interlocking effects at high pressures. Figure 5 also shows the deviations of the data of Diller and Ball [9] as open squares and of those of Ulybin and Makarushkin [10] as open diamonds. The agreement with the latter, taken at 243.15, 253.15, 273.15, and 293.15 K, is rather good, besides for 293.15 K at the lowest densities, as can also be seen in Fig. 1. The viscosity values of Diller and Ball are taken at the same temperatures as ours and at 233.2 K but they are generally a few percent higher than ours, especially those taken at 230 and 233 K.

This investigation was undertaken at the request of the Subcommittee of the IUPAC Commission I.2 on Transport Properties of Fluids in order to provide supplementary data for the improvement of representative equations for the viscosity of carbon dioxide which had already been developed [14]. For liquid, this equation consists in effect of one linear relation

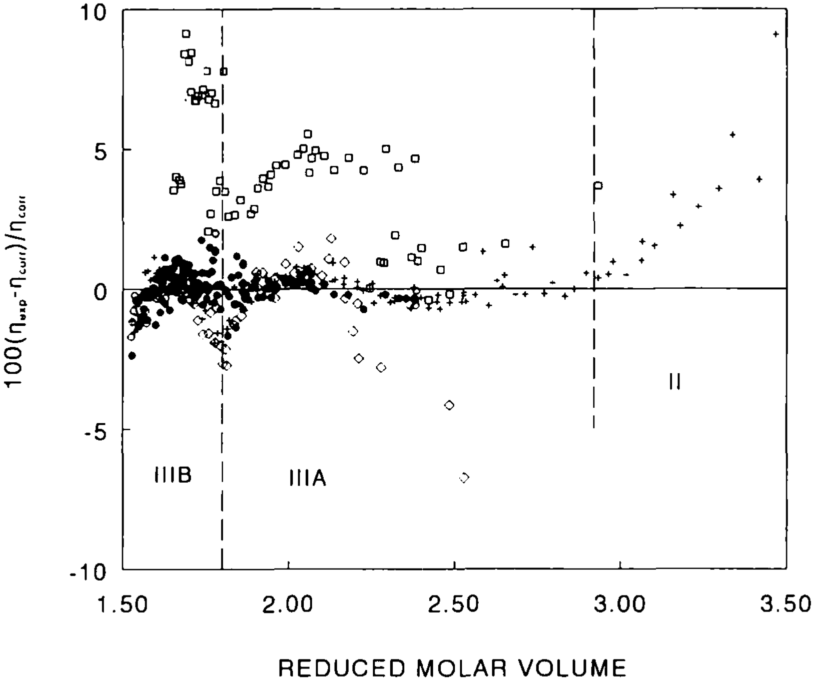

Fig. 5. Percentage deviations of the viscosity coefficient of carbon dioxide from the linear relations shown in Fig. 4 as a function of reduced molar volume: (●) in the stable state; (○) in the metastable state; (+) earlier reported data [8]; (□) Diller and Ball [9]; (◇) Ulybin and Makarushkin [10].

between fluidity and molar volume. The deviation of our data from this equation amounts to about 7% within its validity range and up to 20% outside this range at high pressures. It is remarkable that this relation describes the viscosity at 220 K within 0.5%!

3. CONCLUSION

The main conclusion of this investigation may be drawn from the linear relation between the viscosity coefficient and the pressure, namely, that the common factor in these phenomena must be the number of collisions between the molecules, in accordance with classical concepts. This number is inversely proportional to the available free volume $V - V_B$ according to the linear relation between the fluidity and the molar volume. The value of the viscosity coefficient of simple liquids is then determined by the number of collisions per unit of time and volume and the temperature-dependent efficiency in momentum exchange during a collision. At low densities the molecules are no longer locked in by their neighbors; they can pass by each other and the concept of mean free path length becomes meaningful. The momentum is then transported by traveling molecules and, on collision, simply handed over; in this way the viscosity becomes independent of the density and pressure in first approximation.

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