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Viscosity Measurements on Gaseous Argon, Krypton, and Propane[1]

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A new vibrating-wire viscometer was designed to perform quasi-absolute measurements of very high precision on gases. It was applied to determine the viscosity of argon at temperatures of 298.15, 348.15, and 423.15 K and pressures up to 20 MPa, and the viscosity of krypton at 298.15 and 348.15 K and pressures up to 16 MPa. Furthermore, several isothermal series of viscosity measurements on gaseous propane were carried out. The subcritical isotherms at 298.15, 323.15, 348.15, and 366.15 K were restricted to 95% of the saturated vapor pressure, the supercritical isotherms at 373.15, 398.15, and 423.15 K to 20 MPa. In general, the measurements are characterized by a reproducibility of ±0.05% and an accuracy of ±0.2%. However, close to the critical point an accuracy of ±3% has to be accepted, mainly due to the uncertainty of the density. In this context the influence of the equation of state used for propane is discussed.

KEY WORDS: argon; gas; krypton; measurement; propane; vibrating-wire viscometer; viscosity.

1. INTRODUCTION

In principle, a vibrating-wire viscometer may be an absolute instrument if the wire radius R is precisely known. Only one measurement on a gas with a viscosity coefficient known as accurately as possible for the given thermodynamic state is sufficient to determine the radius. All further measurements can be considered to be quasi-absolute. Viscosity values for argon determined by Kestin and Leidenfrost [1] at 298.15 K with an uncertainty of ±0.15% were used as reference data.

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Measurements on krypton were mainly intended to verify the performance of the calibrated instrument and to compare the results with reliable literature data [2]. The new viscosity measurements on propane, which is an important reference gas for industrial applications, are meant to give a contribution to the development of a more accurate database. Moreover, the supercritical isotherms are to be examined with regard to the kind of density expansion of the viscosity in greater density ranges.

2. APPARATUS

Several improvements of the usual vibrating-wire technique have been implemented to design a highly precise viscometer for measurements on dilute and dense gases [3]. The viscometer cell comprises a Chromel® wire with a nominal radius R of 12.5 μm and a length of 90 mm. Its upper end is clamped between glass blocks, and a brass weight of about 1.1 g is suspended from the lower end. The wire is placed in a magnetic field with 10 mm distance between the magnets and with a flux density of 0.35 T. The vertical length of the field is 60 mm. The optimum ratio between the lengths of the wire and of the field turned out to be 1.5 with regard to the suppression of the third harmonic mode of oscillation. As the arrangement is symmetric, the even harmonics are not expected to be initiated or observed. The oscillation of the wire is initiated by applying a sinusoidal voltage pulse with a frequency close to the resonance frequency of the wire. Since the wire oscillates in a magnetic field, the velocity of the oscillation can be detected by amplifying the induced voltage and measuring it as a function of time. An important feature of the amplifier circuit is its electrical resistance.

According to the Lentzian rule, a force acts on a conductor in a magnetic field opposite to its velocity and proportional to the current. This magnetic damping can be expressed by a magnetic decrement which appears as an additional part of the vacuum decrement Δ_0. To prevent the magnetic part of the damping from becoming too large, the applied amplifier circuit has a resistance of 100 kΩ. Offset suppression filters were left out because they would decrease the amplifier's dynamic qualities. While the oscillation curve is visibly deformed by small-bandwidth amplifiers, distortions by wide-bandwidth amplifiers are not immediately obvious, but appear as an error in the measured decrement Δ. The curve is undistorted without filters, but the offset voltage must be subtracted.

To improve the signal-to-noise ratio, it proved to be useful to carry out 100 acquisitions and to average the measured oscillation curves so that asynchronous noise is minimized. This procedure requires that the recorded oscillation curves are strictly synchronous and that their frequencies do not differ. The synchronization is achieved by the simultaneous start of the initiation pulse and of the acquisition of the oscillation. Furthermore, it was shown experimentally by analyzing 100 single, oscillation curves that the frequencies were nonvarying and that the oscillation parameters had no trend which could indicate a temperature rise by the frequent stimulation of the wire. The temperature rise of one stimulation, caused by the viscous friction as well as by the electric current, was calculated to be smaller than 10^{-5} K and is negligible. The reason for preferring the analysis of averaged curves instead of averaging the oscillation parameters of the single curves, which provides exactly the same results, was simply the smaller time required.

An essential condition for the validity of the measuring theory is a wire displacement much smaller than the radius. Since this is difficult to realize in practice, ω and Δ have to be determined as functions of the amplitude squared. Their correct values are deduced by extrapolation to zero displacement [3]. To obtain the oscillation parameters at different amplitudes, measurements with different initiation voltages can be performed. An alternative procedure is to analyze equally long segments of an oscillation curve. Both ways should provide the same results regardless of the length of the analyzed curve segments. Otherwise, there is an effect of mode coupling, and the wire suspension is consequently to be checked.

The use of Chromel® as the wire material for the instrument is due to its very smooth surface. It has been shown [3] that the rough surface of conventionally used tungsten wire leads to systematic errors.

The experimental equipment (Fig. 1) is intended for measurements at pressures up to 40 MPa. To enable the determination of the decrement and the frequency *in vacuo*, Δ_0 and ω_0, tubes with 5.1 mm inside diameter are used in the vacuum line. Furthermore, the viscometer has been designed without porous or thermally unstable materials. Tubes with 1.5 mm inside

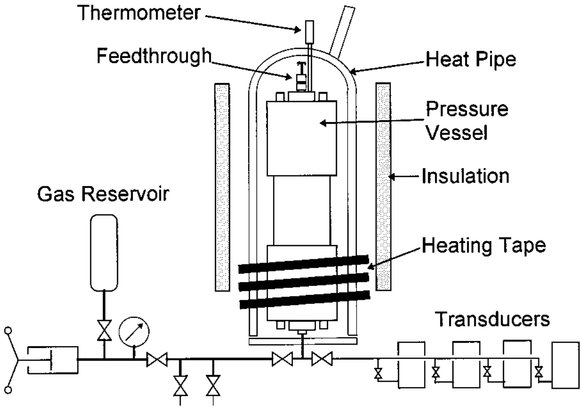

Fig. 1. Schematic of experimental arrangement.

diameter connect the pressure vessel to four pressure transmitters characterized by an uncertainty of 0.01% of reading and 0.01% of full scale. The viscometer cell is attached to the top closure of the vessel. A boron nitride-insulated electrical feedthrough carries the conductors leading to the ends of the wire.

The water-filled heat-pipe thermostat is heated by means of high-temperature heating tape and a 480-W power supply controlled by a PID controller. Temperature measurements are carried out using a premium ITS-90 thermometer and a $6\frac{1}{2}$ digit multimeter. Additional DIN/10-Pt100 sensors are used to check the temperature gradients inside the thermostat.

3. MEASUREMENTS

The procedure of a measurement series started with the determination of the oscillation parameters in vacuo, followed by adding gas up to the maximum pressure. After pressure and temperature were stable within ±0.005% and ±0.01 K, a viscosity measurement was carried out. Then, the gas was partly released for the next measurement point. The vacuum measurement was repeated after the series was completed.

Three isothermal series of measurements on argon at temperatures of 298.15, 348.15, and 423.15 K and pressures up to 20 MPa and two on krypton at temperatures of 298.15 and 348.15 K and pressures up to 16 MPa were carried out. One series comprises about 50 data points. The reproducibility amounts to ±0.02% at pressures below 1 MPa and to ±0.05% at the maximum pressure. At pressures below 0.25 MPa the measured viscosities tend to be too low, which is obviously caused by the slip effect. These data were not included in the evaluation.

The certified purity of the gases supplied by Messer Griesheim, Germany, amounted to 99.998%. The densities were determined using the equation of state by Stewart and Jacobsen [4] for argon and the equation of state by Rabinovich et al. [5] for krypton.

The wire radius R was determined to be 12.770 μm, using reference values for argon by Kestin and Leidenfrost [1] at 0.79 and 1.48 MPa. Measurements on argon at pressures up to 2.8 MPa also agreed with the corresponding data by Kestin and Leidenfrost within ±0.1%. To verify the consistency, a 0.991-m-long specimen of the same wire was weighed. The density was calculated using the calibrated radius and agreed with the density of 8500 $\text{kg} \cdot \text{m}^{-3}$ provided by the supplier to within ±0.1%.

The experimental viscosity values as a function of density were adjusted to isothermal values by means of a first-order Taylor series in terms of temperature. They are recorded in Tables I and II for argon and krypton, respectively.

Table I. Experimental Values of Isotherms for Argon

No.	ρ $(\mathrm{mol \cdot L^{-1}})$	η $(\mu\mathrm{Pa \cdot s})$	No.	ρ $(\mathrm{mol \cdot L^{-1}})$	η $(\mu\mathrm{Pa \cdot s})$	No.	ρ $(\mathrm{mol \cdot L^{-1}})$	η $(\mu\mathrm{Pa \cdot s})$
$T = 298.15$ K								
1	8.4875	30.4670	19	2.7165	24.2620	37	0.65192	22.9227
2	8.2660	30.1726	20	2.5022	24.0995	38	0.56972	22.8775
3	8.0810	29.9180	21	2.3581	23.9870	39	0.49707	22.8380
4	7.6637	29.3673	22	2.2171	23.8890	40	0.48781	22.8401
5	7.2462	28.8345	23	2.0759	23.7917	41	0.40605	22.8008
6	6.8306	28.3262	24	1.9338	23.6980	42	0.36512	22.7790
7	6.3971	27.8161	25	1.7943	23.5969	43	0.32435	22.7575
8	5.9665	27.3316	26	1.6524	23.5030	44	0.28362	22.7389
9	5.5369	26.8690	27	1.5107	23.4129	45	0.24297	22.7225
10	5.1089	26.4201	28	1.3718	23.3284	46	0.20234	22.7031
11	4.6738	25.9635	29	1.2322	23.2413	47	0.16178	22.6828
12	4.2383	25.5631	30	1.1486	23.1913	48	0.14156	22.6759
13	4.0160	25.3519	31	1.0654	23.1470	49	0.12128	22.6632
14	3.7962	25.1581	32	1.0268	23.1208	50	0.10098	22.6503
15	3.5807	24.9741	33	0.98233	23.0979	51[a]	0.082775	22.6381
16	3.3661	24.7814	34	0.89959	23.0553	52[a]	0.080808	22.6371
17	3.1496	24.6071	35	0.81684	23.0075	53[a]	0.060176	22.6197
18	2.9328	24.4377	36	0.73420	22.9654	54[a]	0.041464	22.6014
$T = 348.15$ K								
1	6.9085	31.4522	19	2.2704	26.9767	36	0.55480	25.9341
2	6.5778	31.0530	20	2.0953	26.8495	37	0.48488	25.8965
3	6.4627	30.9122	21	1.9719	26.7617	38	0.41569	25.8657
4	6.2471	30.6560	22	1.8586	26.6872	39	0.34633	25.8344
5	5.9109	30.2880	23	1.7446	26.6148	40	0.31150	25.8154
6	5.5710	29.9194	24	1.6247	26.5331	41	0.27691	25.7982
7	5.2321	29.5667	25	1.5097	26.4662	42	0.24221	25.7837
8	4.8886	29.2044	26	1.3933	26.3896	43	0.20754	25.7724
9	4.5454	28.8853	27	1.2764	26.3244	44	0.17296	25.7549
10	4.1975	28.5427	28	1.1590	26.2544	45	0.15560	25.7455
11	3.8498	28.2267	29	1.0430	26.1850	46	0.13831	25.7398
12	3.5006	27.9285	30	0.97269	26.1500	47	0.12098	25.7332
13	3.3241	27.7757	31	0.90270	26.1121	48	0.10367	25.7232
14	3.1486	27.6364	32	0.83168	26.0738	49[a]	0.086420	25.7156
15	2.9739	27.4986	33	0.76367	26.0394	50[a]	0.069100	25.7014
16	2.7976	27.3591	34	0.69385	26.0017	51[a]	0.051875	25.6881
17	2.6222	27.2276	35	0.62424	25.9692	52[a]	0.034360	25.6506
18	2.4457	27.0983						

Table I. *(Continued)*

No.	ρ $(\mathrm{mol \cdot L^{-1}})$	η $(\mu\mathrm{Pa \cdot s})$	No.	ρ $(\mathrm{mol \cdot L^{-1}})$	η $(\mu\mathrm{Pa \cdot s})$	No.	ρ $(\mathrm{mol \cdot L^{-1}})$	η $(\mu\mathrm{Pa \cdot s})$
$T = 423.15$ K								
1	5.5014	33.9928	19	1.9784	30.9875	37	0.45422	30.1311
2	5.4619	33.9750	20	1.8380	30.9059	38	0.39772	30.1033
3	5.2328	33.7341	21	1.6991	30.8161	39	0.34077	30.0756
4	4.9640	33.4496	22	1.6038	30.7516	40	0.28424	30.0512
5	4.7066	33.2025	23	1.5060	30.6901	41	0.25571	30.0421
6	4.4423	32.9495	24	1.4153	30.6365	42	0.22728	30.0346
7	4.1754	32.7022	25	1.3225	30.5784	43	0.19891	30.0183
8	3.9081	32.4753	26	1.2274	30.5330	44	0.17055	30.0041
9	3.6332	32.2403	27	1.1337	30.4775	45	0.14209	29.9946
10	3.6167	32.2219	28	1.0371	30.4239	46	0.12788	29.9853
11	3.3584	32.0015	29	0.94585	30.3777	47	0.11369	29.9806
12	3.0898	31.7963	30	0.85133	30.3290	48	0.099379	29.9702
13	2.8139	31.5774	31	0.79498	30.2977	49	0.085258	29.9605
14	2.6727	31.4772	32	0.73776	30.2660	50[a]	0.073511	29.9559
15	2.5355	31.3732	33	0.68094	30.2434	51[a]	0.071047	29.9504
16	2.3981	31.2771	34	0.62324	30.2162	52[a]	0.056871	29.9322
17	2.2579	31.1786	35	0.56801	30.1878	53[a]	0.042413	29.9125
18	2.1178	31.0821	36	0.51136	30.1589	54[a]	0.029401	29.8919

[a] Influenced by slip.

In the case of propane the subcritical isotherms at 298.15, 323.15, 348.15, and 366.15 K cover a pressure range up to 95% of the vapor pressure, and the supercritical isotherms at 373.15, 398.15, and 423.15 K extend up to 20 MPa. Propane with a certified purity of 99.95% was used. The density calculation was based on an equation of state made available by Span and Wagner [6] and is to be further discussed. Viscosities measured at subcritical temperatures and pressures close to the vapor pressure were rejected due to their deviations of up to 2% from preliminary correlation curves. Since these deviations were always positive, but not reproducible, an effect of condensation can be supposed. The slip effect appeared to be weaker, so only data obtained at pressures below 0.15 MPa had to be excluded from the evaluation. The reproducibility was the same as for argon, apart from data for densities near the critical density. The viscosity values for these data are characterized by a scatter of $\pm 0.2\%$.

Since the measuring theory [7] provides two working equations which include the viscosity η as well as the density ρ, it is possible to determine both quantities simultaneously from measurements of Δ, Δ_0, ω, and

Table II. Experimental Values of Isotherms for Krypton

No.	ρ $(\mathrm{mol \cdot L^{-1}})$	η $(\mu\mathrm{Pa \cdot s})$	No.	ρ $(\mathrm{mol \cdot L^{-1}})$	η $(\mu\mathrm{Pa \cdot s})$	No.	ρ $(\mathrm{mol \cdot L^{-1}})$	η $(\mu\mathrm{Pa \cdot s})$
				$T = 298$ K				
1	8.8297	42.0910	20	2.1093	27.4712	39	0.41047	25.6631
2	8.2640	40.4202	21	1.9089	27.2164	40	0.36990	25.6303
3	7.6544	38.7172	22	1.7469	27.0263	41	0.32691	25.5933
4	7.1947	37.4679	23	1.6397	26.8924	42	0.28586	25.5660
5	6.7226	36.2634	24	1.4669	26.6960	43	0.24260	25.5348
6	6.3357	35.2973	25	1.3739	25.5851	44	0.20249	25.5024
7	5.8256	34.1219	26	1.2789	26.4836	45	0.18118	25.4790
8	5.3556	33.1076	27	1.1872	26.3897	46	0.15915	25.4603
9	4.9570	32.2644	28	1.1046	26.3093	47	0.14179	25.4498
10	4.6472	31.6205	29	1.0208	26.2243	48	0.12044	25.4353
11	4.2351	30.8428	30	0.92691	26.1264	49	0.10262	25.4187
12	3.9274	30.2623	31	0.83785	26.0414	50[a]	0.079625	25.3961
13	3.6366	29.7613	32	0.75634	25.9647	51[a]	0.063901	25.3773
14	3.3279	29.2428	33	0.68121	25.9045	52[a]	0.050417	25.3651
15	3.0691	28.8366	34	0.62653	25.8524	53[a]	0.041270	25.3488
16	2.8740	28.5409	35	0.57873	25.8017	54[a]	0.029598	25.3223
17	2.6007	28.1498	36	0.53854	25.7756	55[a]	0.021366	25.2979
18	2.4482	27.9211	37	0.49424	25.7348			
19	2.2726	27.6915	38	0.45018	25.6943			
				$T = 348$ K				
1	6.4293	39.4943	19	1.7057	30.8388	37	0.34963	29.4176
2	6.1381	38.8062	20	1.5748	30.6735	38	0.31579	29.3854
3	5.7685	37.9612	21	1.4484	30.5212	39	0.27703	29.3549
4	5.3997	37.1497	22	1.3364	30.3946	40	0.24159	29.3172
5	5.0537	36.4074	23	1.1769	30.2115	41	0.20772	29.2982
6	4.7154	35.7307	24	1.0682	30.0992	42	0.17549	29.2720
7	4.4166	35.1314	25	0.99756	30.0271	43	0.15640	29.2557
8	4.1107	34.5279	26	0.91692	29.9496	44	0.13711	29.2409
9	3.8331	34.0422	27	0.84756	29.8760	45	0.12066	29.2319
10	3.5963	33.6346	28	0.77882	29.8161	46	0.10164	29.2062
11	3.2578	33.0412	29	0.69486	29.7213	47	0.087073	29.1979
12	3.0216	32.6747	30	0.62797	29.6651	48[a]	0.068353	29.1733
13	2.8039	32.3292	31	0.57300	29.6184	49[a]	0.051267	29.1526
14	2.6049	32.0532	32	0.52343	29.5667	50[a]	0.040574	29.1365
15	2.3815	31.7021	33	0.48511	29.5306	51[a]	0.031191	29.1146
16	2.1736	31.4444	34	0.45393	29.4996	52[a]	0.022564	29.0842
17	2.0010	31.2075	35	0.41567	29.4668			
18	1.8315	30.9818	36	0.38008	29.4402			

[a] Influenced by slip.

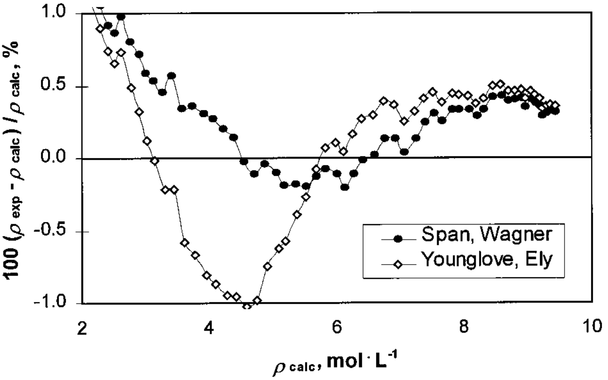

Fig. 2. Deviations of the experimental densities of propane at 398.15 K (this work) from densities calculated with equations of state by Span and Wagner [6] and by Younglove and Ely [8].

ω_0 and a knowledge of R and of the densities of the wire and the weight. However, this method is difficult to apply for measurements on gases, and the viscometer would have to be redesigned to reach an acceptable precision. Although the experimental values for ρ obtained with our viscometer are not satisfactorily precise in the complete density range, they seem to be of sufficient accuracy to demonstrate which equation of state describes the range around the critical density ($5\,\mathrm{mol \cdot L^{-1}}$) more reliably. Figure 2 shows considerable differences between two equations of state, although they are probably based on the same experimental data.

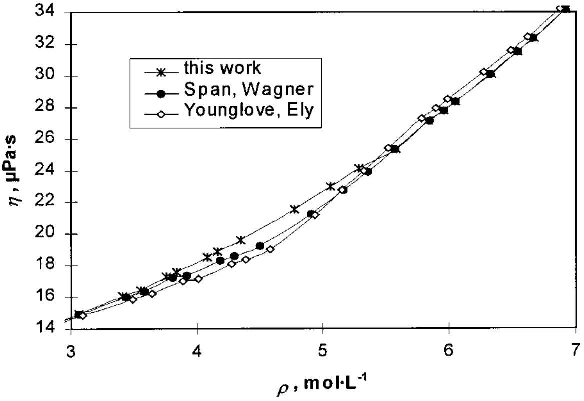

Fig. 3. Viscosity of propane at 373.15 K using experimental densities from this work and densities from equations of state by Span and Wagner [6] and by Younglove and Ely [8].

The influence of the density from equations of state or from our experiments is demonstrated in Fig. 3 for the viscosity isotherm at 373.15 K for propane. The curve shows anomalous behavior near 4.5 $\mathrm{mol \cdot L^{-1}}$ if the Younglove–Ely equation [8] is used, and it becomes a little less in the case of the Span–Wagner equation [6].

The experimental values for propane will be published in a future paper.

4. CORRELATION

A power series representation was assumed for the density dependence of the viscosity. It was restricted to the second [Eq. (1)] or to the third power [Eq. (2)], depending on the considered density range. Due to the slip effect, only a few data were usable in the range of the initial density dependence, so the results of linear fits are not shown here. We used

$$\eta = \eta_0 + \eta_1 \rho + \eta_2 \rho^2 \tag{1}$$

$$\eta = \eta_0 + \eta_1 \rho + \eta_2 \rho^2 + \eta_3 \rho^3 \tag{2}$$

The fits were carried out by means of a multiple linear least-squares analysis. Weighting factors of η^{-2} were chosen to minimize the relative deviations and to calculate the standard deviation σ as a percentage. The coefficients η_i $(0 \leqslant i \leqslant 3)$ generated with the fits of Eqs. (1) and (2) are summarized in Table III for argon and in Table IV for krypton. The density $\rho_{\max}$ is the maximum of the evaluated density range.

The zero-density viscosity coefficients η_0 for argon are compared in Table V with experimental data measured by Kestin et al. [9] and by Vogel [10] by means of oscillating-disk viscometers as well as with viscosity coefficients calculated for an HFD (Hartree–Fock dispersion) potential recommended by Aziz and Slaman [11]. Similarly, η_0 values for krypton are compared in the same table with data measured by van den Berg [2] with a capillary viscometer and by Vogel [10] as well as with HFD viscosity values calculated by Aziz and Slaman [12]. The mutual agreement with the experimental data and calculated values for both gases is within $\pm 0.2\%$ for all temperatures. This illustrates the high accuracy of the experimental data of the present paper.

In Figs. 4–6, differences between experimental data from various sources and viscosities calculated with the fitted cubic correlations are plotted. Figure 4 shows that the viscosity coefficients by Kestin et al. [9] are consistent with our data at moderately low densities, but differ significantly at densities above 2 $\mathrm{mol \cdot L^{-1}}$. It is assumed that the procedure by Kestin et al. to extend the working range of their viscometer using an extrapolated

Table III. Coefficients of Eqs. (1) and (2) for Argon

T (K)	$\rho_{\max}$ ($\mathrm{mol \cdot L^{-1}}$)	η_0 ($\mu\mathrm{Pa \cdot s}$)	$10^3\eta_1$ ($\mu\mathrm{Pa \cdot s \cdot L \cdot mol^{-1}}$)	$10^3\eta_2$ ($\mu\mathrm{Pa \cdot s \cdot L^2 \cdot mol^{-2}}$)	$10^3\eta_3$ ($\mu\mathrm{Pa \cdot s \cdot L^3 \cdot mol^{-3}}$)	σ (%)
298.15	3.1	22.610 ± 0.001	436 ± 2	63.2 ± 0.7		0.012
	8.5	22.607 ± 0.002	444 ± 2	62.3 ± 0.8	-0.65 ± 0.07	0.021
348.15	2.5	25.680 ± 0.001	418 ± 2	66.5 ± 0.8		0.008
	6.9	25.677 ± 0.001	426 ± 2	64.8 ± 0.9	-0.82 ± 0.09	0.014
423.15	3.1	29.931 ± 0.001	413 ± 2	61.6 ± 0.8		0.011
	5.5	29.931 ± 0.002	412 ± 3	63.9 ± 1.6	-0.77 ± 0.31	0.014

Table IV. Coefficients of Eqs. (1) and (2) for Krypton

T (K)	$\rho_{\max}$ ($\mathrm{mol \cdot L^{-1}}$)	η_0 ($\mu\mathrm{Pa \cdot s}$)	$10^3\eta_1$ ($\mu\mathrm{Pa \cdot s \cdot L \cdot mol^{-1}}$)	$10^3\eta_2$ ($\mu\mathrm{Pa \cdot s \cdot L^2 \cdot mol^{-2}}$)	$10^3\eta_3$ ($\mu\mathrm{Pa \cdot s \cdot L^3 \cdot mol^{-3}}$)	σ (%)
298.15	2.9	25.347 ± 0.002	716.6 ± 2.5	138.0 ± 1.0		0.015
	8.8	25.347 ± 0.002	714.7 ± 2.1	140.3 ± 0.7	-0.73 ± 0.23	0.023
348.15	2.2	29.133 ± 0.002	756.3 ± 3.9	140.6 ± 1.5		0.014
	6.4	29.133 ± 0.002	754.7 ± 3.6	142.7 ± 1.3	-1.44 ± 0.47	0.023

Table V. Comparison of Zero-Density Coefficients (μPa · s)

T (K)	This work	Kestin et al. [9] or Van den Berg [2]	Δ (%)	Vogel [10]	Δ (%)	HFD	Δ (%)
Argon							
298.15	22.610	22.608 [9]	−0.01	22.592	−0.08	22.61 [11]	0.00
348.15	25.680			25.665	−0.06	25.66 [11]	−0.08
423.15	29.931			29.912	−0.06	29.94 [11]	0.03
Krypton							
298.15	25.347	25.349 [2]	0.01	25.373	0.10	25.39 [12]	0.17
348.15	29.133	29.061 [2]	−0.25	29.173	0.14	29.18 [12]	0.16

[a] $\Delta = 100(\eta_{\text{Lit}} - \eta_{\text{this work}})/\eta_{\text{this work}}$.

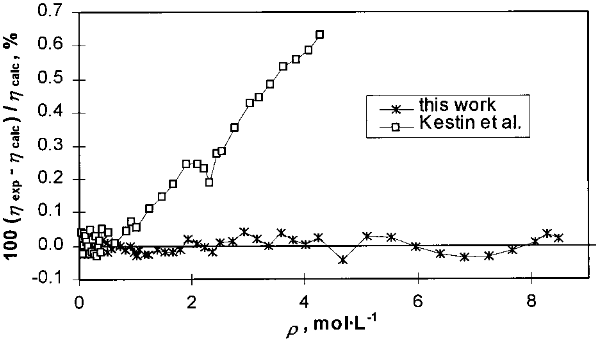

Fig. 4. Deviations of experimental viscosities for argon at 298.15 K (this work and Kestin et al. [9]) from the cubic correlation (Table III).

calibration function is incorrect. Figures 5 and 6 show that there are much smaller deviations between our values and the highly accurate data by van den Berg [2] for krypton at 298.15 and 348.15 K. Taking into account the difference of the η_0 values at 348.15 K, the deviations are approximately $\pm 0.1\%$ with different trends at each temperature. This indicates that there are not significant systematic errors in the measurement technique used in the present paper.

Alternatively, the following logarithmic density expansion was tested to represent the isotherms:

$$\eta = \eta_0 + \eta_1 \rho + \eta_2 \rho^2 + \eta_2' \rho^2 \ln(\rho) \tag{3}$$

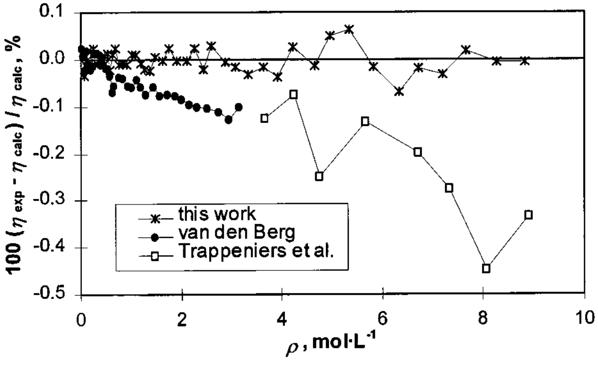

Fig. 5. Deviations of experimental viscosities for krypton at 298.15 K (this work, van den Berg [2], Trappeniers et al. [13]) from the cubic correlation (Table IV).

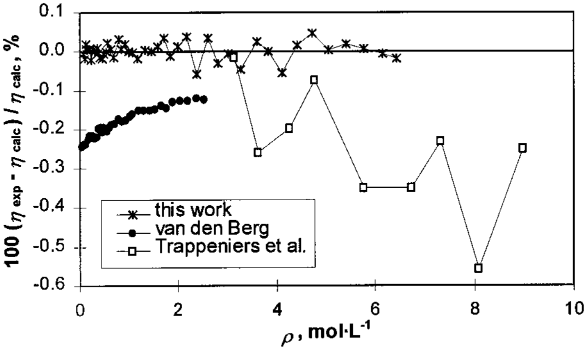

Fig. 6. Deviations of experimental viscosities for krypton at 348.15 K (this work, van den Berg [2], Trappeniers et al. [13]) from the cubic correlation (Table IV).

The standard deviations σ of the fits are shown as functions of the maximum density $\rho_{\max}$ in Fig. 7 for argon and in Fig. 8 for krypton. It is evident from both figures that an additional term to the quadratic term is needed. However, it cannot be decided whether this must be a cubic or a logarithmic term. The results of the corresponding fits for the data by Kestin et al. [9] for argon are plotted in Fig. 9. It is obvious that no further term beyond the quadratic is needed within the rather limited density range. Finally, Fig. 10 shows the analogous plots for krypton at 298.15 K that follows from an evaluation of the measurements by van den Berg [2] and Trappeniers et al. [13]. The density range of the data by van den Berg is again too small to justify the need for more than three

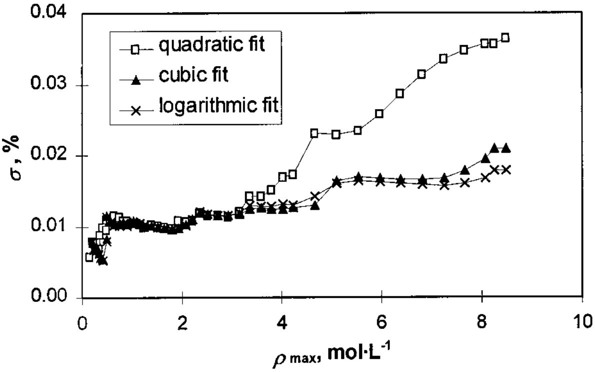

Fig. 7. Standard deviation of fits at 298.15 K for argon (this work).

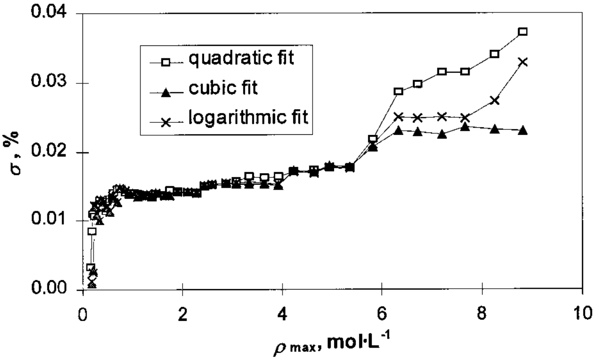

Fig. 8. Standard deviation of fits at 298.15 K for krypton (this work).

parameters. If the data by Trappeniers et al. are included, the situation is not significantly improved due to the large scatter of these values.

The correlation results for the subcritical isotherms of propane are presented in Table VI, and those for the supercritical isotherms in Table VII. While the isotherms at 348.15 and 366.15 K can be represented using both Eqs. (2) and (3), for the isotherms above the critical temperature of 369.82 K, one more term is needed to obtain consistent parameters as shown in Table VII:

$$\eta = \eta_0 + \eta_1 \rho + \eta_2 \rho^2 + \eta_3 \rho^3 + \eta_4 \rho^4 \tag{4}$$

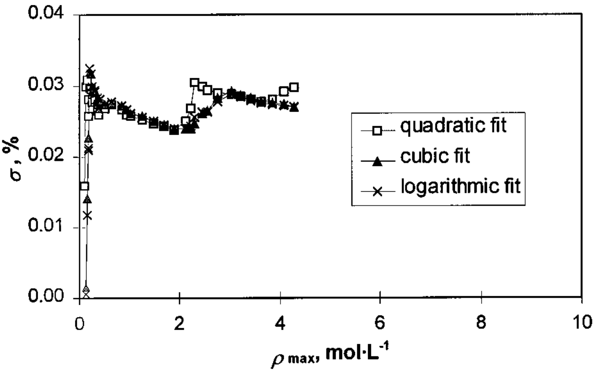

Fig. 9. Standard deviation of fits at 298.15 K for argon by Kestin et al. [9].

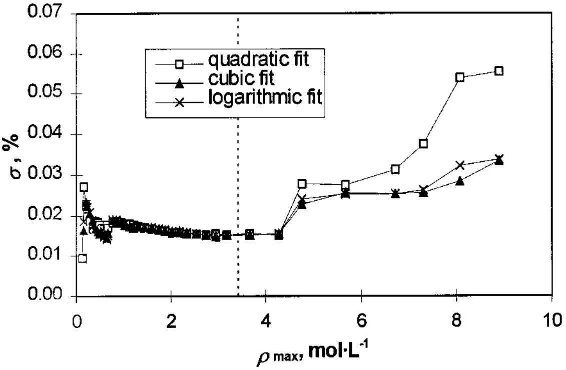

Fig. 10. Standard deviation of fits at 298.15 K for krypton incorporating data by van den Berg [2] (0.04 to 3.2 mol · L^{-1}) and Trappeniers et al. [13] (3.7 to 8.9 mol · L^{-1}).

If the logarithmic term is involved, two more parameters are needed to reach a convergent function $\sigma(\rho_{\max})$ for the supercritical series of measurements:

$$\eta = \eta_0 + \eta_1 \rho + \eta_2 \rho^2 + \eta_2' \rho^2 \ln(\rho) + \eta_3 \rho^3 + \eta_3' \, \rho^3 \ln(\rho) \tag{5}$$

But the coefficients η_0, η_1, η_2, and η_2' generated with Eq. (5) are inconsistent with values obtained with Eq. (3) in the density range below 2 mol · L^{-1}. Therefore, the results of the logarithmic fits are not presented here. The logarithmic fits can only provide reasonable results if the logarithmic term is followed by a fifth-power term instead of the cubic term, but this seems unreasonable from a theoretical point of view:

$$\eta = \eta_0 + \eta_1 \rho + \eta_2 \rho^2 + \eta_2' \rho^2 \ln(\rho) + \eta_5 \rho^5 \tag{6}$$

The high values of σ for the supercritical isotherms of propane are probably caused by the uncertainty of the equation of state in the vicinity of the critical density. When using the equation of state by Younglove and Ely [8], σ increases to 1.1% at 373.15 K, to 0.22% at 398.15 K (Fig. 11), and to 0.11% at 423.15 K. This shows that the equation of state by Span and Wagner [6] is more accurate than the Younglove–Ely equation in this region.

5. CONCLUSION

Measurements over wide density ranges were carried out with a new vibrating-wire viscometer. High precision is achieved provided that the gas

Table VI. Coefficients of Eqs. (1) and (2) for Subcritical Propane

T (K)	$\rho_{\max}$ (mol · L^{-1})	η_0 (μPa · s)	$10^3\eta_1$ (μPa · s · L · mol^{-1})	$10^3\eta_2$ (μPa · s · L^2 · mol^{-2})	$10^3\eta_3$ (μPa · s · L^3 · mol^{-3})	σ (%)
298.15	0.5	8.141 ± 0.001	−128 ± 6	580 ± 13		0.011
323.15	0.8	8.808 ± 0.001	26 ± 5	540 ± 6		0.022
348.15	0.8	9.459 ± 0.001	195 ± 3	496 ± 5		0.013
	1.5	9.458 ± 0.001	197 ± 5	518 ± 9	−40.1 ± 4.0	0.019
366.15	0.9	9.931 ± 0.001	272 ± 3	459 ± 3		0.014
	2.6	9.929 ± 0.001	286 ± 4	455 ± 4	−13.7 ± 1.1	0.030

Table VII. Coefficients of Eqs. (1) and (2), and (4) for Supercritical Propane

T (K)	$\rho_{\max}$ (mol · L^{-1})	η_0 (μPa · s)	$10^3\eta_1$ (μPa · s · L · mol^{-1})	$10^3\eta_2$ (μPa · s · L^2 · mol^{-2})	$10^3\eta_3$ (μPa · s · L^3 · mol^{-3})	$10^3\eta_4$ (μPa · s · L^4 · mol^{-4})	σ (%)
373.15	0.8	10.114 ± 0.001	358 ± 3	430 ± 4			0.012
	1.6	10.113 ± 0.001	363 ± 5	435 ± 7	−18.9 ± 3.1		0.018
	10.1	10.103 ± 0.014	418 ± 35	390 ± 21	−16.6 ± 4.1	3.44 ± 0.24	0.556
398.15	0.8	10.768 ± 0.001	382 ± 4	485 ± 5			0.014
	1.6	10.768 ± 0.001	376 ± 6	524 ± 9	−46.0 ± 4.0		0.019
	9.4	10.772 ± 0.002	367 ± 5	515 ± 3	−43.6 ± 0.6	4.93 ± 0.04	0.072
423.15	0.9	11.398 ± 0.001	451 ± 4	484 ± 4			0.015
	1.6	11.398 ± 0.001	443 ± 6	527 ± 10	−47.8 ± 4.5		0.019
	8.6	11.402 ± 0.002	428 ± 5	528 ± 3	−49.0 ± 0.8	5.29 ± 0.05	0.063

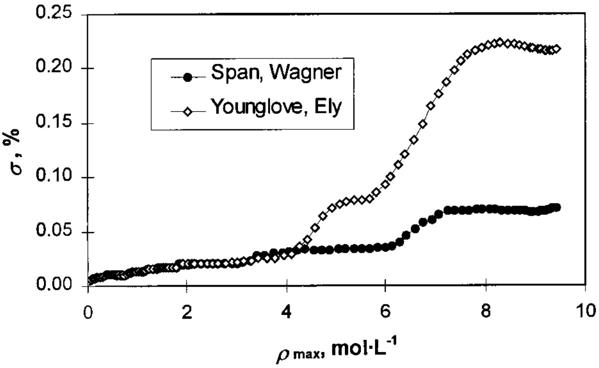

Fig. 11. Standard deviation of a fourth-power fit at 398.15 K for propane based on the equations of state by Span and Wagner [6] and by Younglove and Ely [8].

density is available from a reliable source. A power series in the density proved to give an appropriate representation for the experimental viscosity data. It can be inferred that, if logarithmic terms exist, their influence is rather small, so they could not be found when the density is not accurately known.

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REFERENCES

1. J. Kestin and W. Leidenfrost, *Physica* **25**:1033 (1959).
2. H. R. van den Berg, Precisiemetingen aan de Viscositeitscoefficient van Krypton en de logarithmische Term in de Dichtheidsontwikkeling, Ph.D. thesis (University of Amsterdam, 1979).
3. J. Wilhelm, E. Vogel, J. K. Lehmann, and W. A. Wakeham, *Int. J. Thermophys.* **19**:391 (1998).
4. R. B. Stewart and R. T. Jacobsen, *J. Phys. Chem. Ref. Data* **18**:639 (1989).
5. V. A. Rabinovich, A. A. Vasserman, V. I. Nedustup, and L. S. Veksler, *Thermophysical Properties of Neon, Argon, Krypton, and Xenon*, National Standard Reference Data Service of the USSR, Vol. 10 (Hemisphere Publishing, New York, 1988).
6. R. Span and W. Wagner, to be submitted to *Int. J. Thermophys.*
7. T. Retsina, S. M. Richardson, and W. A. Wakeham, *Appl. Sci. Res.* **43**:325 (1987).
8. B. A. Younglove and J. F. Ely, *J. Phys. Chem. Ref. Data* **16**:577 (1987).

9. J. Kestin, E. Paycoc, and J. V. Sengers, *Physica* **54**:1 (1971).
10. E. Vogel, *Ber. Bunsenges. Phys. Chem.* **88**:997 (1984).
11. R. A. Aziz and M. J. Slaman, *J. Chem. Phys.* **92**:1030 (1990).
12. R. A. Aziz and M. J. Slaman, *Chem. Eng. Comm.* **78**:153 (1989).
13. N. J. Trappeniers, A. Botzen, J. van Oosten, and H. R. van den Berg, *Physica* **31**:945 (1965).