896 *J. Chem. Eng. Data* **2005,** *50,* 896−906

Viscosity Measurements on Gaseous Sulfur Hexafluoride

Jörg Wilhelm,[†] Daniel Seibt,[†] Eckard Bich,[†] Eckhard Vogel,[*,†] and Egon Hassel[‡]

Institut für Chemie, Universität Rostock, D-18059 Rostock, Germany, and Lehrstuhl für Technische
Thermodynamik, Universität Rostock, D-18059 Rostock, Germany

A vibrating-wire viscometer of very high precision was used to measure the viscosity coefficient of gaseous sulfur hexafluoride. The experimental data were taken at subcritical temperatures of (300 and 316) K up to 90% of the saturated vapor pressure and at supercritical temperatures of (321, 333.15, 350, 375, 400, and 425) K at pressures up to 20 MPa. The measuring values were evaluated using an equation of state by Wagner and Kurzeja. The reproducibility is ±(0.05 to 0.1)%, whereas the total uncertainty is estimated to be ±(0.25 to 0.4)% with a distinct increase approaching the critical region. The viscosity values of the isotherms were evaluated using a power series expansion in terms of density without and with logarithmic term. The existence of a quadratic term that is logarithmic in density could not be proven. A comparison with data from the literature shows that the new values agree in the low-density range within ±0.2% and at higher densities apart from the near-critical region within ±0.3% with the most reliable data.

Introduction

Thermodynamic properties of sulfur hexafluoride have been investigated rather frequently because of its importance in the semiconductor processing industry as a surrogate gas and in electrical engineering as an insulation material. The most recent equations of state for thermodynamic properties of sulfur hexafluoride were reported by Hurly et al.[1] and by Wagner and Kurzeja.[2] However, the transport property data are not of the same high accuracy as the thermodynamic data. Although Trengove and Wakeham[3] as well as Strehlow and Vogel[4] presented so-called individual correlations for the viscosity in the limit of zero density in a reasonable database, the representation by Altunin[5] for the complete viscosity surface of the fluid suffered from the limited number of experimental data and their uncertainties. Consequently, there is a permanent demand for new high-precision values and for their correlation connected with a critical assessment of the available data.

Furthermore, sulfur hexafluoride is of theoretical interest as a globular molecule with an octahedral structure. Hence, there were attempts to include it in an extended theorem of corresponding states[6] as well as to determine its intermolecular potential in a reasonable manner.[7−9] Both ways were used to derive thermodynamic and transport properties of sulfur hexafluoride.[6,10,11] Although these papers have been limited to two-body interaction and to the so-called zero-density transport properties, they are the basis for any investigation at higher densities related to many-body interactions.

A vibrating-wire viscometer designed by Wilhelm et al.[12] to perform measurements of very high precision on gases was recently applied to determine the viscosity of argon, krypton, and propane between (298 and 423) K up to a maximum pressure of 20 MPa.[13,14] The measuring program was then extended to methane and two natural gases[15−17] in a thermodynamic range that is of particular interest to the gas industry.

Here, eight isothermal series of measurements on gaseous sulfur hexafluoride, two at subcritical and six at supercritical temperatures, were carried out to give a contribution to the development of a more accurate database for the transport property surfaces of this substance with industrial and scientific importance.

Experimental Section

Only the essential features of the instrument are given because Wilhelm et al.[12] and Wilhelm and Vogel[13] have already reported the details. The wire is placed in a magnetic field in such a manner that even harmonics cannot be initiated because of the symmetric arrangement of the wire and field and the third harmonic mode of the oscillation is suppressed using a ratio of 1.5 between the lengths of wire and field. The wire material has been chosen to be Chromel because the rough surface of tungsten mostly used for liquids causes systematic errors in measurements on dilute and even on dense gases. The oscillation is initiated by a sinusoidal voltage pulse with a frequency close to the resonance frequency of the wire. The oscillation following the pulse is detected by amplifying the induced voltage and measuring it as a function of time. To improve the signal-to-noise ratio, 100 runs are recorded, and the measured oscillation curves are averaged. Although the measuring theory requires small displacements y on the order of 1% of the wire radius R, comparably large displacements are applied to obtain reasonably large measuring signals. Because the parameters of the oscillation curves, the logarithmic decrement Δ and the frequency ω, depend on the square of the relative initial amplitude $\epsilon = y_{\max}/R$, different values of ϵ are used in several oscillation runs to derive the correct values of Δ and ω by extrapolation as a function of $\epsilon^2 \rightarrow 0$.

The viscometer cell is suspended from the top closure of a pressure vessel that is placed in a heat-pipe thermostat and is connected with four pressure transmitters supplied

---

[*] To whom correspondence should be addressed. E-mail: eckhard.vogel@uni-rostock.de. Tel: +49-381-4986510. Fax: +49-381-4986502.

[†] Institut für Chemie, Universität Rostock.

[‡] Lehrstuhl für Technische Thermodynamik, Universität Rostock.

10.1021/je049612f CCC: $30.25 © 2005 American Chemical Society
Published on Web 02/25/2005

by Digiquartz. Their working ranges of (0.69, 2.76, 13.8, and 41.4) MPa are characterized by uncertainties of 0.01% in the reading and 0.01% of the full scale. The temperature is determined by means of a premium ITS-90 thermometer and a 6 $^1/_2$ digit multimeter with an uncertainty of ±0.015 K.

According to the working equations resulting from the theory of the vibrating-wire viscometer,[18] the viscosity η can be calculated from the measured values Δ and ω under the condition that the density ρ of the fluid, the density ρ_s and the radius R of the wire, and the parameters of the oscillation in vacuo Δ_0 and ω_0 are known. An accurate wire radius R cannot be obtained by direct measurements. Hence, it has been determined to be (12.770 ± 0.005) μm by means of viscosity measurements on argon at room temperature with reference values by Kestin and Leidenfrost[19] assuming the density of the wire material Chromel to be 8500 kg·m^{-3} as given by the supplier.

Measurements and Results

The subcritical isotherms of the measurements on sulfur hexafluoride at (300 and 316) K cover ranges up to 90% of the saturated vapor pressure, whereas the supercritical isotherms at (321, 333.15, 350, 375, 400, and 425) K extend up to 20 MPa. The certified purity of sulfur hexafluoride supplied by Messer Griesheim (Germany) was 99.995%. The densities ρ were calculated from the measured pressures p and temperatures T with the equation of state by Wagner and Kurzeja.[2]

The isothermal series of measurements partially comprise more than 100 data points. The individual points were not measured exactly at the nominal temperatures, but the deviations of the experimental temperatures were kept within ±0.1 K. Hence, the experimental viscosity values could be adjusted to isothermal values by means of a linear correction. Nevertheless, a Taylor expansion restricted to the second power in temperature was used for that purpose. In this procedure, the densities directly derived from the experiments and those for the isotherms are the same. Then the pressures at the nominal temperatures of the isotherms were recalculated from the densities. The results for all series of measurements are listed in Table 1. Because of the large number of experimental points, only the pressures, densities, and viscosities are given in the Table. We are aware of the fact that the densities should possibly be reevaluated with an improved equation of state that might be available in the future. For such a reevaluation, the exact experimental temperatures and pressures as well as Δ and ω are needed. Because the measurements on propane[14] and methane[16] have shown that experimental values at pressures below 0.1 MPa could be influenced by the slip effect, such data were critically inspected. However, only three values were identified to be influenced by slip. They are included and marked in the Table but excluded from further evaluation.

The reproducibility of most measurements is less than ±0.05%. Furthermore, errors arising from the uncertainty of the calibration values[19] and the density calculation have to be considered. The uncertainty of the density propagates into that of the viscosity in two ways. The density is immediately needed in the working equations to obtain the viscosity from the measured values Δ and ω. In addition, the viscosity is a function of density. In general, an uncertainty of 0.2% of the density data contributes a change of 0.1% in the viscosity only. As a result, the total uncertainties of the viscosity values are conservatively estimated to be ±0.25% for $\rho < 3$ mol·L^{-1} and ±0.4% for higher densities, but the uncertainty is distinctly increased when the critical region is approached, as shown in the next section for the 321 K isotherm in the reduced density range of $0.8 \le \delta \le 1.2$.

Analysis

The experimental results of the isotherms were correlated as a function of the reduced density δ by means of a power series representation restricted to the sixth power or lower depending on the included density range.

$$\eta(\tau, \delta) = \sum_{i=0}^{n} \eta_i(\tau)\delta^i \tag{1}$$

$$\delta = \frac{\rho}{\rho_{c,SF_6}} \qquad \rho_{c,SF_6} = 5.0813\ \text{mol·L}^{-1}$$

$$\tau = \frac{T}{T_{c,SF_6}} \qquad T_{c,SF_6} = 318.7232\ \text{K}$$

Weighting factors of $(100/\eta)^2$ were used in the multiple linear least-squares regression to minimize the relative deviations. The weighted standard deviation σ related to the maximum density of the experimental points included in the fit by means of eq 1 was used as a criterion for the description of the considered isotherm.

Figure 1 shows that for the 316 K isotherm, which includes experimental values up to 2.05 mol·L^{-1}, a series expansion according to eq 1 (open symbols) that is fourth order in reduced density δ is needed. Analogously in Figure 2, it is evident for the 333.15 K isotherm that a series expansion that is sixth order in δ is appropriate to describe all experimental points up to molar densities of 9.15 mol·L^{-1}. In addition, this Figure illustrates that the standard deviation σ seems to be slightly increased in the density range of $4 < \rho/\text{mol·L}^{-1} < 7$, possibly by small uncertainties in the temperatures and pressures directly measured and needed for the densities. However, only a few points are characterized by deviations of ±(0.1 to 0.2)% from the fit, which is noticeable alone in comparison with the high reproducibility of the measurements. As a consequence, we have had a closer look at the 321 K isotherm, which is closest to the critical temperature. The deviations of the experimental points from the fit, again using a series expansion that is sixth order in δ, are given in Figure 3. It is obvious that comparably large deviations of $\pm 0.2 < \Delta/\% < \pm 0.8$ occur, mainly in the density range of $3 < \rho/\text{mol·L}^{-1} < 7$. Therefore, a number of experimental data from this density range were excluded in a new fit so that the deviations for the experimental points included were within ±0.2%. The results are also shown in Figure 3. Here, the experimental data of the density range of $3.8 < \rho/\text{mol·L}^{-1} < 6.1$ deviate systematically up to −1.7%. These data excluded from the fit are marked in Table 1. The reason for the increases in the reproducibility up to ±0.1% and in the uncertainty up to ±(1.5 to 2.0)% is that close to the critical point small uncertainties in the measured pressures and temperatures lead to high uncertainties in the calculated densities because of the strong compressibility in this thermodynamic region. We believe that probably all of the viscosity measurements, in which the density was derived on the basis of temperature and pressure measurements, suffer from the same difficulty, although most authors claim a comparably low uncertainty, even in the near-critical region.

The power of δ in the series expansion needed for all eight isotherms and the values of the coefficients η_i are

Table 1. Experimental Viscosity Values of Sulfur Hexafluoride along Isotherms

p / MPa	ρ / mol·L^{-1}	η / μPa·s	p / MPa	ρ / mol·L^{-1}	η / μPa·s	p / MPa	ρ / mol·L^{-1}	η / μPa·s
				$T = 300$ K				
2.0393	1.1471	16.698	1.0902	0.50352	15.647	0.44452	0.18764	15.384
1.9800	1.0955	16.592	1.0364	0.47468	15.615	0.42572	0.17928	15.378
1.9273	1.0515	16.502	0.99776	0.45429	15.593	0.40157	0.16862	15.374
1.8651	1.0018	16.406	0.96874	0.43915	15.577	0.37855	0.15850	15.371
1.8265	0.97183	16.348	0.93075	0.41955	15.557	0.35341	0.14753	15.364
1.7844	0.94006	16.292	0.89841	0.40306	15.543	0.32730	0.13620	15.359
1.7353	0.90405	16.225	0.86995	0.38868	15.532	0.30145	0.12506	15.354
1.6806	0.86509	16.162	0.83589	0.37164	15.513	0.27858	0.11526	15.350
1.6373	0.83503	16.109	0.80020	0.35399	15.494	0.25151	0.10373	15.349
1.5946	0.80607	16.061	0.76398	0.33626	15.482	0.22752	0.093585	15.343
1.5377	0.76848	16.005	0.73145	0.32050	15.468	0.19525	0.080005	15.338
1.4933	0.73986	15.961	0.70096	0.30587	15.457	0.17762	0.072631	15.334
1.4179	0.69255	15.890	0.66510	0.28883	15.449	0.15262	0.062234	15.329
1.3809	0.66992	15.858	0.63458	0.27446	15.440	0.12570	0.051101	15.328
1.3333	0.64133	15.818	0.59798	0.25739	15.426	0.10589	0.042950	15.324
1.2806	0.61034	15.778	0.56524	0.24227	15.416	0.073624	0.029756	15.316
1.2236	0.57757	15.737	0.53831	0.22993	15.410	0.050936	0.020535	15.313
1.1815	0.55377	15.704	0.49153	0.20870	15.395	0.026358	0.010597	15.294[a]
1.1401	0.53079	15.680	0.47171	0.19979	15.393			
				$T = 316$ K				
3.1352	2.0475	20.246	1.7242	0.80224	16.891	0.68507	0.27913	16.199
3.0700	1.9513	19.919	1.6672	0.76903	16.839	0.65085	0.26421	16.183
3.0079	1.8675	19.626	1.6098	0.73630	16.775	0.61448	0.24848	16.169
2.9811	1.8332	19.504	1.5727	0.71549	16.742	0.58501	0.23582	16.162
2.9165	1.7545	19.252	1.5304	0.69207	16.712	0.54834	0.22019	16.150
2.8609	1.6910	19.057	1.4656	0.65679	16.651	0.51948	0.20798	16.140
2.7927	1.6173	18.832	1.4229	0.63392	16.623	0.49091	0.19596	16.130
2.7243	1.5478	18.621	1.3744	0.60828	16.584	0.46839	0.18654	16.126
2.6582	1.4840	18.442	1.3143	0.57710	16.535	0.42801	0.16976	16.113
2.5872	1.4189	18.264	1.2573	0.54798	16.496	0.40243	0.15920	16.106
2.5100	1.3516	18.087	1.2152	0.52683	16.463	0.38376	0.15153	16.104
2.4485	1.3002	17.958	1.1783	0.50846	16.442	0.35770	0.14087	16.097
2.3758	1.2419	17.814	1.1204	0.48001	16.406	0.33206	0.13044	16.092
2.3191	1.1980	17.712	1.0841	0.46240	16.384	0.30735	0.12044	16.083
2.2732	1.1635	17.630	1.0311	0.43696	16.355	0.28746	0.11243	16.079
2.2238	1.1272	17.548	0.99472	0.41974	16.336	0.26284	0.10255	16.074
2.1552	1.0783	17.437	0.95592	0.40154	16.311	0.24503	0.095437	16.073
2.0874	1.0315	17.333	0.91390	0.38202	16.289	0.21805	0.084708	16.066
2.0216	0.98738	17.253	0.88281	0.36770	16.280	0.19759	0.076609	16.063
1.9885	0.96560	17.203	0.84320	0.34962	16.259	0.17460	0.067546	16.058
1.9227	0.92336	17.110	0.81074	0.33494	16.244	0.14354	0.055369	16.053
1.8603	0.88426	17.041	0.78040	0.32131	16.229	0.11275	0.043364	16.046
1.8211	0.86023	16.997	0.74905	0.30734	16.220			
1.7725	0.83086	16.942	0.71263	0.29123	16.201			
				$T = 321$ K				
11.075	9.4924	129.72	3.7936	3.2184	25.995	1.4318	0.62226	16.856
10.352	9.3869	125.81	3.7654	3.0983	25.298	1.3862	0.59904	16.819
9.5481	9.2575	121.16	3.7292	2.9663	24.624	1.3400	0.57582	16.785
8.6475	9.0932	115.39	3.6956	2.8597	24.073	1.2824	0.54724	16.744
7.9051	8.9371	110.50	3.6514	2.7362	23.455	1.2232	0.51832	16.699
7.2562	8.7796	105.68	3.6061	2.6246	22.937	1.1787	0.49688	16.670
6.3887	8.5236	98.449	3.5583	2.5196	22.445	1.1250	0.47129	16.636
5.9380	8.3592	94.160	3.4988	2.4025	21.946	1.0894	0.45456	16.618
5.5541	8.1929	90.007	3.4459	2.3083	21.562	1.0314	0.42757	16.580
5.1340	7.9676	84.736	3.3844	2.2082	21.166	0.96900	0.39894	16.550
4.8791	7.7957	80.934	3.2820	2.0590	20.602	0.93423	0.38317	16.536
4.7405	7.6848	78.593	3.2296	1.9895	20.352	0.89620	0.36607	16.517
4.6013	7.5554	76.060	3.1366	1.8753	19.952	0.85752	0.34883	16.499
4.4655	7.4041	73.046	3.0500	1.7774	19.625	0.82355	0.33381	16.481
4.3494	7.2446	69.998	2.9591	1.6821	19.324	0.79088	0.31947	16.465
4.2238	7.0180	65.989	2.8735	1.5982	19.082	0.73246	0.29409	16.444
4.1600	6.8646	63.504	2.8039	1.5336	18.875	0.68118	0.27207	16.427
4.1129	6.7218	61.250	2.6881	1.4323	18.596	0.63322	0.25170	16.412
4.0771	6.5854	59.016	2.6295	1.3837	18.459	0.59218	0.23442	16.393
4.0468	6.4397	56.834	2.5819	1.3453	18.368	0.56316	0.22229	16.384
4.0208	6.2773	54.475	2.5347	1.3082	18.262	0.52386	0.20598	16.372
4.00116	6.1142	52.136[b]	2.4513	1.2448	18.118	0.48899	0.19162	16.361

Table 1. (Continued)

p / MPa	ρ / mol·L^{-1}	η / μPa·s	p / MPa	ρ / mol·L^{-1}	η / μPa·s	p / MPa	ρ / mol·L^{-1}	η / μPa·s
				$T = 321$ K				
3.9883	5.9763	50.176^b	2.3732	1.1878	17.974	0.45731	0.17866	16.353
3.9770	5.8235	48.130^b	2.3327	1.1590	17.895	0.42898	0.16714	16.344
3.9688	5.6817	46.379^b	2.2703	1.1157	17.796	0.40093	0.15579	16.337
3.9610	5.5163	44.346^b	2.2213	1.0825	17.717	0.37489	0.14532	16.332
3.9554	5.3739	42.717^b	2.1204	1.0161	17.580	0.33965	0.13122	16.321
3.9506	5.2358	41.314^b	2.0419	0.96636	17.471	0.29339	0.11286	16.313
3.9457	5.0824	39.950^b	2.0049	0.94342	17.426	0.26410	0.10132	16.301
3.9384	4.8457	37.433^b	1.9307	0.89830	17.336	0.23958	0.091706	16.298
3.9333	4.6898	36.146^b	1.8938	0.87632	17.295	0.20562	0.078464	16.291
3.9266	4.5083	34.808^b	1.8474	0.84907	17.240	0.16996	0.064645	16.286
3.9184	4.3231	33.549^b	1.7886	0.81518	17.177	0.14657	0.055634	16.282
3.9101	4.1693	32.182^b	1.7445	0.79012	17.128	0.11416	0.043207	16.274
3.8994	4.0065	31.041^b	1.6931	0.76143	17.080	0.09702	0.036663	16.268
3.8878	3.8643	29.901^b	1.6470	0.73610	17.031	0.07746	0.029221	16.266
3.8585	3.5970	28.265	1.5389	0.67802	16.938			
3.8196	3.3482	26.745	1.4833	0.64887	16.894			
				$T = 333.15$ K				
12.565	9.1507	118.35	4.4069	3.2756	27.148	1.3669	0.55699	17.366
11.412	8.9624	112.24	4.3282	3.1051	26.158	1.3078	0.52973	17.318
10.465	8.7837	106.74	4.2399	2.9331	25.244	1.2332	0.49579	17.271
9.8020	8.6413	102.66	4.1482	2.7720	24.449	1.1674	0.46632	17.229
9.1068	8.4715	97.949	4.0508	2.6175	23.703	1.0925	0.43327	17.181
8.5198	8.3065	93.546	3.9321	2.4475	22.910	1.0257	0.40419	17.148
7.9000	8.1025	88.688	3.8154	2.2967	22.289	0.94643	0.37021	17.101
7.3783	7.8971	83.953	3.7220	2.1856	21.849	0.88792	0.34545	17.075
6.9506	7.6951	79.524	3.6051	2.0566	21.352	0.83779	0.32447	17.053
6.6277	7.5137	75.839	3.5040	1.9528	20.967	0.77231	0.29736	17.027
6.3382	7.3206	72.174	3.3987	1.8512	20.602	0.71774	0.27501	17.000
6.0982	7.1296	68.701	3.3061	1.7667	20.318	0.67118	0.25612	16.982
5.8695	6.9098	64.834	3.1952	1.6709	20.007	0.63615	0.24201	16.972
5.7099	6.7251	61.963	3.0894	1.5842	19.734	0.59065	0.22382	16.954
5.5674	6.5298	58.832	3.0083	1.5207	19.550	0.54764	0.20676	16.939
5.4475	6.3352	56.104	2.8720	1.4187	19.251	0.50660	0.19060	16.925
5.3436	6.1370	53.309	2.7663	1.3435	19.042	0.47964	0.18005	16.917
5.2549	5.9402	50.722	2.6319	1.2521	18.801	0.44340	0.16594	16.908
5.1788	5.7471	48.331	2.5192	1.1789	18.620	0.41693	0.15569	16.902
5.1094	5.5488	46.033	2.4277	1.1216	18.479	0.37894	0.14106	16.890
5.0490	5.3582	43.946	2.2947	1.0412	18.283	0.35089	0.13032	16.880
4.9916	5.1628	41.896	2.0257	0.88823	17.951	0.31941	0.11832	16.870
4.9332	4.9523	39.824	1.9670	0.85640	17.902	0.29403	0.10869	16.863
4.8801	4.7542	38.012	1.9174	0.82990	17.832	0.27520	0.10158	16.860
4.8281	4.5591	36.290	1.8535	0.79628	17.778	0.24322	0.089542	16.851
4.7766	4.3691	34.756	1.7729	0.75465	17.691	0.21878	0.080388	16.846
4.7258	4.1878	33.308	1.7058	0.72062	17.629	0.19848	0.072809	16.838
4.6718	4.0050	31.855	1.6297	0.68271	17.568	0.17242	0.063119	16.834
4.6123	3.8175	30.544	1.5664	0.65172	17.508	0.14252	0.052050	16.825
4.5496	3.6350	29.384	1.5028	0.62104	17.460	0.11358	0.041388	16.819
4.4797	3.4500	28.190	1.4197	0.58166	17.397	0.091552	0.033302	16.814
				$T = 350$ K				
12.301	8.2716	93.858	4.5981	2.5521	24.429	1.3927	0.52932	18.108
11.424	8.0614	88.692	4.4732	2.4296	23.863	1.3412	0.50761	18.066
10.614	7.8348	83.544	4.3073	2.2760	23.220	1.2654	0.47604	18.027
9.8234	7.5712	78.141	4.1430	2.1331	22.612	1.1965	0.44772	17.982
9.2940	7.3623	73.987	3.9875	2.0056	22.114	1.1462	0.42721	17.955
8.8495	7.1597	70.284	3.8695	1.9133	21.793	1.0515	0.38908	17.903
8.5587	7.0097	67.540	3.7480	1.8220	21.460	0.99788	0.36772	17.872
8.2974	6.8605	65.050	3.6554	1.7548	21.228	0.95425	0.35049	17.840
8.0062	6.6744	62.180	3.5044	1.6493	20.852	0.90026	0.32932	17.820
7.7673	6.5031	59.567	3.4053	1.5826	20.643	0.85504	0.31173	17.798
7.5920	6.3645	57.547	3.3196	1.5266	20.469	0.80998	0.29433	17.787
7.4081	6.2057	55.315	3.2245	1.4659	20.283	0.77989	0.28277	17.775
7.2300	6.0369	53.062	3.1253	1.4043	20.098	0.73948	0.26733	17.755
7.0765	5.8785	51.077	3.0471	1.3568	19.959	0.70164	0.25296	17.746
6.9188	5.7021	48.914	2.9782	1.3158	19.860	0.65426	0.23508	17.719
6.7696	5.5217	46.840	2.9004	1.2704	19.712	0.61951	0.22204	17.714
6.6354	5.3482	44.968	2.7984	1.2122	19.569	0.57970	0.20718	17.689
6.5108	5.1779	43.191	2.6577	1.1342	19.359	0.55281	0.19720	17.683

Table 1. (Continued)

p	ρ	η	p	ρ	η	p	ρ	η
MPa	$\text{mol}\cdot\text{L}^{-1}$	$\mu\text{Pa}\cdot\text{s}$	MPa	$\text{mol}\cdot\text{L}^{-1}$	$\mu\text{Pa}\cdot\text{s}$	MPa	$\text{mol}\cdot\text{L}^{-1}$	$\mu\text{Pa}\cdot\text{s}$
$T = 350$ K								
6.3851	4.9977	41.393	2.6081	1.1073	19.291	0.52275	0.18608	17.674
6.2808	4.8429	39.947	2.5051	1.0525	19.164	0.48530	0.17230	17.660
6.1776	4.6859	38.568	2.4492	1.0233	19.084	0.45038	0.15952	17.654
6.0676	4.5155	37.056	2.3940	0.99477	19.028	0.41850	0.14790	17.646
5.9562	4.3417	35.607	2.3093	0.95170	18.934	0.39050	0.13774	17.632
5.8500	4.1762	34.343	2.1086	0.85263	18.705	0.36313	0.12784	17.624
5.7410	4.0082	32.986	2.0432	0.82120	18.641	0.33244	0.11679	17.610
5.6388	3.8536	31.894	2.0059	0.80347	18.607	0.29524	0.10346	17.599
5.5242	3.6848	30.782	1.9646	0.78402	18.565	0.26903	0.094109	17.598
5.4313	3.5520	29.949	1.8883	0.74842	18.493	0.23801	0.083086	17.586
5.3274	3.4085	29.018	1.8400	0.72617	18.445	0.20456	0.071248	17.583
5.2087	3.2511	28.056	1.7132	0.66876	18.346	0.17068	0.059314	17.565
5.0961	3.1085	27.237	1.6563	0.64342	18.302	0.14377	0.049872	17.564
4.9643	2.9498	26.366	1.6218	0.62817	18.269	0.11761	0.040727	17.549
4.8483	2.8172	25.714	1.5461	0.59504	18.213	0.09654	0.033386	17.547
4.7329	2.6915	25.084	1.4731	0.56356	18.159	0.06467	0.022318	17.530[a]
$T = 375$ K								
16.802	8.0443	89.996	5.5354	2.6195	26.171	1.1468	0.39135	19.045
15.713	7.8355	85.265	5.2809	2.4423	25.346	1.0676	0.36270	19.008
14.447	7.5554	79.480	5.0570	2.2926	24.668	0.99957	0.33826	18.968
13.867	7.4103	76.553	4.8210	2.1408	24.012	0.91796	0.30921	18.936
13.213	7.2309	73.194	4.5990	2.0035	23.480	0.85526	0.28709	18.903
12.730	7.0857	70.444	4.3843	1.8757	22.994	0.80508	0.26949	18.879
12.235	6.9242	67.796	4.1366	1.7339	22.489	0.74670	0.24914	18.857
11.466	6.6409	63.216	3.9607	1.6369	22.142	0.69512	0.23128	18.837
11.030	6.4600	60.520	3.6997	1.4979	21.672	0.66140	0.21965	18.822
10.547	6.2384	57.382	3.4184	1.3546	21.223	0.61298	0.20303	18.799
10.221	6.0743	55.189	3.2141	1.2545	20.946	0.56393	0.18629	18.779
9.8689	5.8834	52.751	3.0525	1.1776	20.721	0.53914	0.17787	18.777
9.5737	5.7109	50.648	2.8792	1.0971	20.512	0.49973	0.16451	18.764
9.2577	5.5130	48.364	2.5873	0.96622	20.188	0.46482	0.15274	18.753
8.9729	5.3228	46.317	2.4843	0.92130	20.062	0.43536	0.14283	18.740
8.7113	5.1383	44.477	2.3993	0.88474	19.979	0.40352	0.13216	18.733
8.4527	4.9470	42.589	2.3006	0.84284	19.905	0.37136	0.12142	18.722
8.2020	4.7540	40.792	2.0430	0.73610	19.663	0.34215	0.11170	18.710
7.9731	4.5720	39.193	1.9666	0.70515	19.594	0.30836	0.10049	18.705
7.7629	4.4011	37.702	1.8851	0.67245	19.538	0.28280	0.092034	18.696
7.5244	4.2039	36.121	1.8095	0.64244	19.481	0.25830	0.083955	18.688
7.2935	4.0111	34.659	1.7233	0.60861	19.412	0.21998	0.071357	18.676
7.0929	3.8432	33.432	1.5883	0.55634	19.320	0.18332	0.059352	18.656
6.8876	3.6722	32.239	1.5344	0.53570	19.280	0.15674	0.050676	18.650
6.6777	3.4990	31.115	1.4609	0.50780	19.238	0.13208	0.042649	18.644
6.3262	3.2153	29.385	1.3850	0.47925	19.190	0.10302	0.033216	18.643
6.0004	2.9620	27.909	1.3025	0.44854	19.140	0.072559	0.023358	18.617[a]
5.7786	2.7956	27.061	1.2113	0.41490	19.087			
$T = 400$ K								
19.958	7.6869	83.860	6.0166	2.4218	26.577	1.0256	0.32184	20.056
18.718	7.4692	79.395	5.7427	2.2785	25.936	0.97298	0.30463	20.033
17.814	7.2939	75.995	5.4607	2.1345	25.309	0.93059	0.29082	20.011
16.792	7.0755	72.010	5.1932	2.0012	24.766	0.85397	0.26600	19.980
15.882	6.8598	68.401	4.8985	1.8582	24.207	0.81844	0.25455	19.964
15.061	6.6446	64.860	4.5641	1.7009	23.626	0.79141	0.24586	19.950
14.342	6.4374	61.792	4.1529	1.5145	22.982	0.75374	0.23378	19.935
13.719	6.2415	59.012	3.8641	1.3882	22.562	0.70250	0.21742	19.910
12.979	5.9861	55.667	3.6142	1.2819	22.252	0.66990	0.20705	19.899
12.397	5.7656	52.948	3.4637	1.2191	22.052	0.63633	0.19639	19.889
11.902	5.5641	50.548	3.2663	1.1382	21.838	0.56964	0.17532	19.865
11.434	5.3603	48.273	3.0217	1.0402	21.564	0.52038	0.15983	19.844
11.000	5.1600	46.186	2.8354	0.96718	21.379	0.48284	0.14807	19.831
10.589	4.9606	44.287	2.5394	0.85386	21.093	0.45870	0.14052	19.822
10.191	4.7584	42.339	2.4742	0.82935	21.040	0.43142	0.13202	19.812
9.8332	4.5700	40.704	2.3498	0.78300	20.929	0.38716	0.11826	19.798
9.4835	4.3800	39.026	1.9560	0.63988	20.628	0.35606	0.10862	19.785
9.1399	4.1888	37.499	1.8764	0.61158	20.566	0.31657	0.096416	19.772
8.7990	3.9955	36.041	1.7680	0.57341	20.487	0.27692	0.084202	19.761
8.4906	3.8185	34.750	1.6885	0.54565	20.435	0.24997	0.075924	19.752
8.1420	3.6169	33.321	1.6157	0.52038	20.392	0.22470	0.068178	19.748

Table 1. (Continued)

$\frac{p}{\text{MPa}}$	$\frac{\rho}{\text{mol·L}^{-1}}$	$\frac{\eta}{\mu\text{Pa·s}}$	$\frac{p}{\text{MPa}}$	$\frac{\rho}{\text{mol·L}^{-1}}$	$\frac{\eta}{\mu\text{Pa·s}}$	$\frac{p}{\text{MPa}}$	$\frac{\rho}{\text{mol·L}^{-1}}$	$\frac{\eta}{\mu\text{Pa·s}}$
				$T = 400$ K				
7.8339	3.4385	32.163	1.4625	0.46781	20.292	0.20050	0.060776	19.734
7.5530	3.2763	31.149	1.3974	0.44571	20.252	0.17448	0.052833	19.727
7.2410	3.0974	30.088	1.3197	0.41948	20.215	0.15361	0.046473	19.716
6.9507	2.9329	29.173	1.2409	0.39307	20.170	0.12769	0.038592	19.711
6.6599	2.7705	28.306	1.1533	0.36390	20.123	0.10075	0.030415	19.699
6.3596	2.6057	27.459	1.0882	0.34241	20.089			
				$T = 425$ K				
20.442	6.9899	72.707	6.0564	2.1163	26.541	1.0671	0.31262	21.170
19.579	6.8272	69.925	5.7394	1.9837	26.000	0.99700	0.29141	21.140
18.751	6.6598	67.073	5.4542	1.8664	25.526	0.93966	0.27412	21.108
17.904	6.4756	63.975	5.1246	1.7333	25.013	0.86754	0.25248	21.076
17.025	6.2690	60.940	4.8636	1.6297	24.638	0.81331	0.23628	21.052
16.201	6.0590	58.220	4.5462	1.5060	24.202	0.76424	0.22166	21.030
15.462	5.8561	55.633	4.2988	1.4113	23.879	0.71537	0.20716	21.014
14.767	5.6519	53.091	4.0664	1.3238	23.615	0.66863	0.19333	20.996
14.152	5.4589	50.899	3.7971	1.2241	23.303	0.62986	0.18188	20.980
13.246	5.1537	47.674	3.5861	1.1473	23.074	0.59807	0.17252	20.968
12.731	4.9686	45.794	3.3255	1.0540	22.816	0.55286	0.15925	20.954
12.199	4.7686	43.892	3.1504	0.99224	22.639	0.50316	0.14470	20.931
11.725	4.5837	42.230	2.9311	0.91596	22.436	0.46685	0.13410	20.918
11.563	4.5187	41.706	2.5785	0.79573	22.144	0.42479	0.12185	20.901
10.899	4.2462	39.478	2.4796	0.76253	22.056	0.39273	0.11254	20.889
10.296	3.9893	37.437	2.3442	0.71747	21.957	0.37410	0.10714	20.881
9.8761	3.8063	36.135	1.9205	0.57918	21.663	0.34533	0.098806	20.876
9.5145	3.6465	35.009	1.8335	0.55128	21.605	0.31135	0.088988	20.864
9.1354	3.4774	33.855	1.7576	0.52708	21.554	0.28954	0.082695	20.856
8.7607	3.3093	32.772	1.6563	0.49497	21.491	0.26375	0.075267	20.848
8.3923	3.1435	31.791	1.5876	0.47334	21.448	0.22829	0.065075	20.836
8.0641	2.9959	30.966	1.5063	0.44788	21.406	0.20512	0.058427	20.827
7.7127	2.8384	30.057	1.4428	0.42805	21.366	0.19207	0.054686	20.820
7.3632	2.6828	29.208	1.3856	0.41030	21.332	0.17136	0.048757	20.812
7.0060	2.5252	28.400	1.2994	0.38366	21.289	0.15520	0.044136	20.806
6.6543	2.3719	27.681	1.2134	0.35723	21.244	0.12034	0.034186	20.795
6.3395	2.2364	27.063	1.1415	0.33525	21.209	0.094411	0.026798	20.782

[a] Influenced by slip. [b] Excluded from polynomial fit.

given in Table 2. The Table shows that the temperature dependence of the first density coefficient η_1 is distinctly positive, whereas the higher coefficients seem to be only weakly temperature-dependent.

In addition, the experimental data of the present work were analyzed with a power series expansion including a logarithmic term that is quadratic in density.

$$\eta(\tau, \delta) = \sum_{i=0}^{2} \eta_i(\tau)\delta^i + \eta_2'(\tau)\delta^2 \ln(\delta) + \sum_{i=3}^{n} \eta_i(\tau)\delta^i \qquad (2)$$

The reason for considering an additional term proportional to $\delta^2 \ln(\delta)$ in the series expansion in terms of the reduced

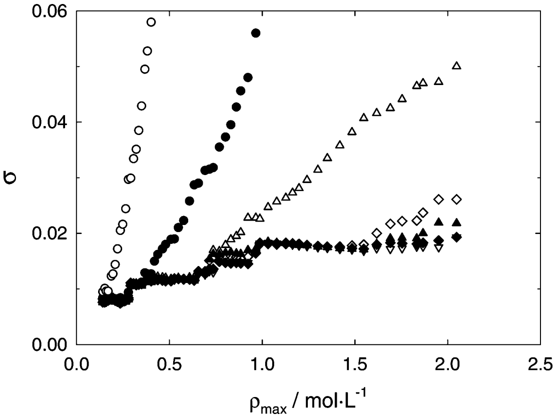

Figure 1. Evaluation of the 316 K isotherm with a power series expansion in reduced density δ (eq 1) as well as with a power series expansion including a logarithmic term that is quadratic in reduced density δ (eq 2). Representation of the weighted standard deviation σ as a function of the maximum molar density $\rho_{\max}$ for which experimental points are included. ○, First order in δ (i = 1) of eq 1; △, second order in δ (i = 2) of eq 1; ◇, third order in δ (i = 3) of eq 1; ▽, fourth order in δ (i = 4) of eq 1; ●, first order in δ (i = 1) of eq 2; ▲, second order in δ (i = 2) of eq 2; ◆, third order in δ (i = 3) of eq 2.

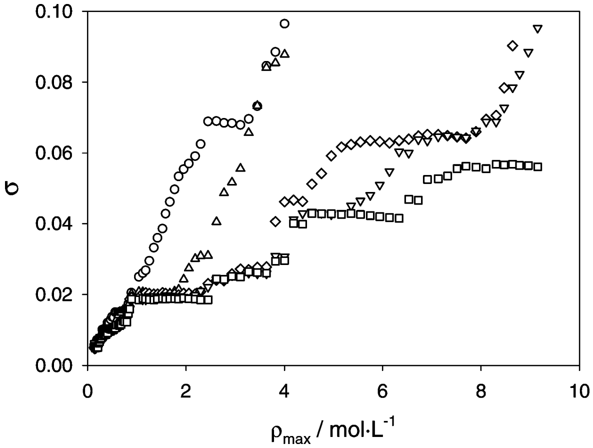

Figure 2. Evaluation of the 333.15 K isotherm with a power series expansion in reduced density δ (eq 1). Representation of the weighted standard deviation σ as a function of the maximum molar density $\rho_{\max}$ for which experimental points are included. ○, Second order in δ (i = 2); △, third order in δ (i = 3); ◇, fourth order in δ (i = 4); ▽, fifth order in δ (i = 5); □, sixth order in δ (i = 6).

Table 2. Coefficients of Equation 1

T/K	n	$\rho_{\max}$/mol·L^{-1}	η_0/μPa·s	η_1/μPa·s	η_2/μPa·s	η_3/μPa·s	η_4/μPa·s	η_5/μPa·s	η_6/μPa·s	σ (weighted)
300	2	1.15	15.309 ± 0.001	1.237 ± 0.029	21.948 ± 0.14					0.023
316	4	2.05	16.035 ± 0.002	1.408 ± 0.063	29.064 ± 0.69	−27.046 ± 2.8	26.675 ± 3.6			0.019
321	6	9.49	16.257 ± 0.003	1.701 ± 0.068	28.586 ± 0.47	−27.018 ± 1.2	35.179 ± 1.5	−18.666 ± 0.8	4.302 ± 0.16	0.046
333.15	6	9.15	16.797 ± 0.003	2.455 ± 0.086	26.592 ± 0.59	−20.271 ± 1.6	24.858 ± 1.9	−12.267 ± 1.1	2.937 ± 0.23	0.056
350	6	8.27	17.530 ± 0.003	2.884 ± 0.092	27.643 ± 0.67	−22.560 ± 1.9	26.828 ± 2.6	−13.279 ± 1.6	3.177 ± 0.36	0.054
375	6	8.04	18.613 ± 0.004	3.782 ± 0.106	26.325 ± 0.81	−19.358 ± 2.4	23.520 ± 3.3	−12.155 ± 2.0	3.141 ± 0.48	0.053
400	6	7.69	19.677 ± 0.003	4.452 ± 0.085	26.801 ± 0.66	−23.084 ± 2.0	30.666 ± 2.9	−17.786 ± 1.9	4.705 ± 0.46	0.038
425	6	6.99	20.763 ± 0.004	5.067 ± 0.133	27.233 ± 1.13	−27.655 ± 3.8	42.366 ± 5.9	−29.754 ± 4.2	8.905 ± 1.10	0.055

density δ has its origin in the fact that the dynamical correlations between molecules persist over distances large compared with the range of the intermolecular potential.[20] Calculations of the η_2' coefficient were performed only for a gas of hard spheres, demonstrating that its value is very small.[21] Attempts to derive the logarithmic term by statistical analysis of accurate experimental viscosity data showed that the coefficient of such a term should also be very small.[22,23] The logarithmic term includes renormalized four-particle contributions related to sequences of successive binary collisions among four particles,[21] and the simple term that is quadratic in density accounts for genuine quadruple collisions.[24] Hence, it is not clear whether the logarithmic term should be arranged in eq 2 before or after the simple term that is quadratic in density. Wilhelm and Vogel[13] discussed the logarithmic term in addition to the simple quadratic term and found that the density ranges of the measurements on argon by Kestin et al.[22] as well as on krypton by van den Berg[23] were obviously too small to justify the need for a further term beyond a quadratic term in a series expansion without a logarithmic term. Furthermore, Wilhelm and Vogel demonstrated that a further term beyond the simple quadratic term was needed for the description of their own measurements on argon and krypton. Here, we restrict our analysis using eq 2 to two isotherms and to a reasonable density range not influenced by the small uncertainties in the pressure and temperature measurements in the near-critical region.

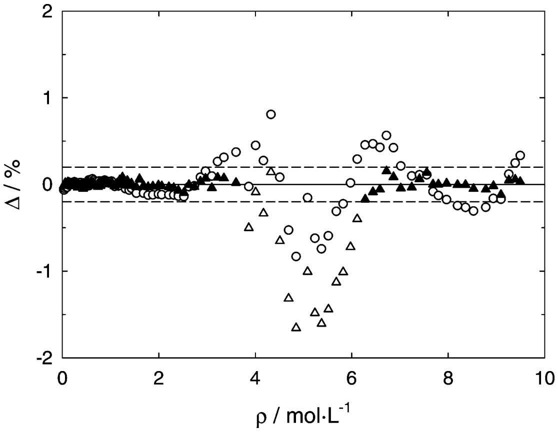

Figure 3. Evaluation of the 321 K isotherm with a power series expansion of sixth order in reduced density δ (eq 1). Deviations [$\Delta = 100(\eta_{\rm expt} - \eta_{\rm fit})/\eta_{\rm fit}$] as a function of molar density ρ. ○, All data included in the fit; ▲, critical region excluded from the fit; △, recalculated points in the critical region.

The standard deviations of the fits with eq 2 are shown in Figure 1 for the 316 K isotherm and in Figure 4 for the restricted 333.15 K isotherm in comparison with the standard deviations of the fits with eq 1. It is evident from both Figures that the representation of the experimental data with the logarithmic term added to the linear term is only slightly improved (filled circles in comparison with open circles), whereas the density range of a description with a small standard deviation could further be extended including a simple term that is quadratic in density (open triangles). If the logarithmic term is taken into account in addition to the simple quadratic term (filled triangles), then the description is marginally better as in the case when a cubic term is considered instead of the logarithmic one (open diamonds). If the number of coefficients η_i needed for an appropriate description is taken as a criterion, then there is practically no difference in the representation using

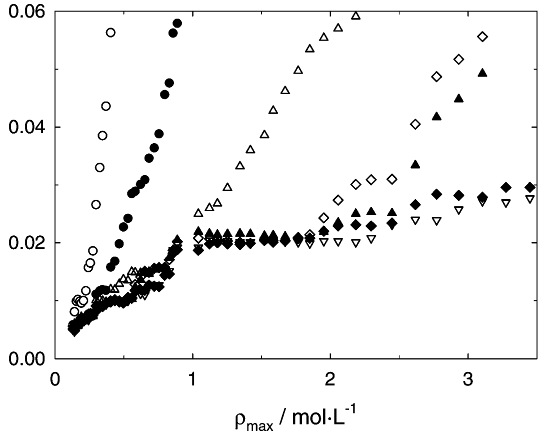

Figure 4. Evaluation of the 333.15 K isotherm at molar densities up to $\rho = 3.5$ mol·L^{-1} with a power series expansion in reduced density δ (eq 1) as well as with a power series expansion including a logarithmic term that is quadratic in reduced density δ (eq 2). Representation of weighted standard deviation σ as a function of maximum molar density $\rho_{\max}$ for which experimental points are included. ○, First order in δ ($i = 1$) of eq 1; △, second order in δ ($i = 2$) of eq 1; ◇, third order in δ ($i = 3$) of eq 1; ▽, fourth order in δ ($i = 4$) of eq 1; ●, first order in δ ($i = 1$) of eq 2; ▲, second order in δ ($i = 2$) of eq 2; ◆, third order in δ ($i = 3$) of eq 2.

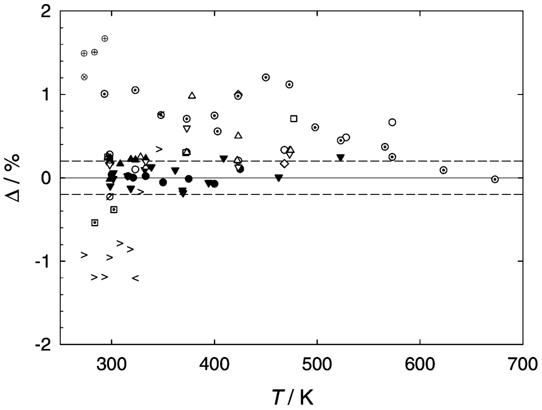

Figure 5. Comparison of experimental low-density viscosity data from the literature and from this paper with the correlation at atmospheric pressure by Strehlow and Vogel.[4] Deviations [$\Delta = 100(\eta_{\mathrm{expt}} - \eta_{\mathrm{cor}})/\eta_{\mathrm{cor}}$] as a function of temperature T. Experimental data: ●, present work; ◆, Kestin et al.;[29] ▼, Timrot et al.;[30] ▲, Hoogland et al.;[31] ø, Berg;[32] ■, Hurly et al.;[33] ○, Hellemans et al.;[34] □, Kestin et al.;[35] △, Kestin et al.;[36] ▽, Kestin et al.;[37] ◇, Abe et al.;[38] ⊙, Dawe et al.;[40] ⊡, Harris et al.;[41] >, Ueda and Kigoshi;[42] <, Tanaka et al.;[43] ⊕, Lukin et al.;[44] ⊗, Lukin et al.[45]

a power series expansion up to the fourth order in density or using an additional logarithmic term in a series expansion up to the third order (five coefficients each). All of this seems to lead to the conclusion that the logarithmic term is without a decisive effect added to the linear term alone. The logarithmic term should be considered after the simple quadratic term or, at least, in connection with this term. Furthermore, the same effectiveness can be achieved when a cubic term is added to a quadratic term instead of the logarithmic one. These results clearly show that for practical purposes, such as the representation of the viscosity surface in all fluid ranges, a power series expansion without a logarithmic term is adequate.

Comparison with Literature

As a reference for comparison at low density, a correlation for atmospheric pressure by Strehlow and Vogel[4] derived from their measurements has been used. The older data by Earwicker and Fear,[25] McCoubrey and Singh,[26] Ellis and Raw,[27] and Raw and Tang,[28] which are measured in capillary viscometers and are somewhat higher, by (2 to 3.5)%, than the values of the correlation by Strehlow and Vogel, were excluded from the comparison. Figure 5 contains the deviations of the more recent experimental data from the literature and of this paper. The Figure shows that the most reliable data,[29–33] including those in this paper, agree with the correlation by Strehlow and Vogel at atmospheric pressure within ±0.2%, although quite different measuring techniques were applied. Kestin et al.[29] Timrot et al.,[30] as well as Strehlow and Vogel used oscillating-disk viscometers operating in a relative manner, whereas Hoogland et al.[31] and Berg[32] used absolute capillary viscometers. Hurly et al.[33] performed their measurements with a relative Greenspan acoustic viscometer. In this paper, a vibrating-wire viscometer was employed in a relative mode. The experimental data by Kestin and coworkers,[34–38] determined at temperatures higher than room temperature, show systematic positive deviations from the correlation by Strehlow and Vogel but also from the other reliable data. This is in agreement with findings for noble and some other gases. The reason for this is a temperature measurement error in the experimental equipment used by Kestin and co-workers, which was extensively discussed by Vogel et al.[39] The higher deviations of the experimental results by Dawe et al.[40] and Harris et al.[41] are due to the aims of these papers directed at measurements at relatively high and low temperatures. The additional measurements at low densities[42–45] can certainly not be considered to be of high precision.

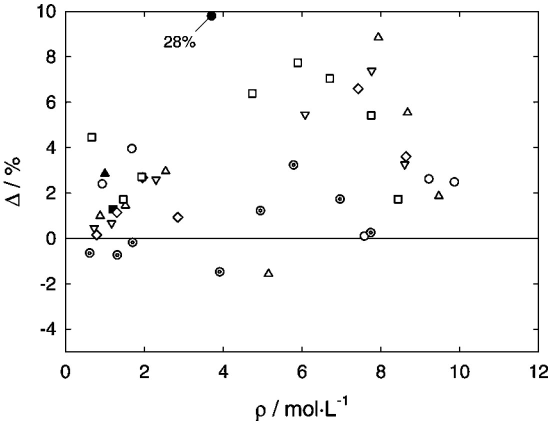

Figure 6. Comparison of experimental viscosity data by Grigoriev et al.[47] at higher densities with the results of this paper according to eq 1 with the coefficients for the highest order in δ from Table 2. Deviations [$\Delta = 100(\eta_{\mathrm{lit}} - \eta_{\mathrm{present}})/\eta_{\mathrm{present}}$] as a function of molar density ρ: ■, 300 K; ▲, 316 K; ○, 321 K; ●, 321 K (outlier); △, 333.15 K; ◇, 350 K; ▽, 375 K; □, 400 K; ⊙, 425 K.

There exist only a limited number of measurements at higher pressures or densities[30,31,33,46–49] apart from that of the present paper. The comparison with our results is made difficult because the evaluation of all measurements required an equation of state that was not the same in different papers. In addition, the data were sometimes given to be dependent on only pressure and temperature, and the measuring temperatures in the reports were also different from that of this paper. To perform a reasonable comparison of the new values with that from literature, we calculated densities for the data by Timrot et al.,[30] Grigoriev et al.,[47] and Hurly et al.,[33] applying the equation of state by Wagner and Kurzeja,[2] whereas in the case of Hoogland et al.[31,46] the densities given by the authors were immediately used. Afterward, all viscosity values with the exception of the data by Hurly et al.[33] were corrected to the corresponding isothermal temperatures of the present work by using the same Taylor expansion procedure as for our experimental points, which means a Taylor expansion restricted to the second power. In the case of Hurly et al., we recalculated our values to the 298.15 K isotherm of that paper.

Figure 6 contains the comparison with the data by Grigoriev et al.[47] limited to the density range of our paper. The data by Grigoriev et al. measured with a capillary viscometer and characterized by an estimated uncertainty of about ±1% are generally higher than our values up to 10%, including one outlier (+28%) near the critical region. These differences distinctly exceed the mutual uncertainties of both experimental techniques. Although Grigoriev et al. extended their measurements to higher temperatures and pressures than those in this paper, their data can certainly not be used as reference values for a viscosity surface to be developed.

In Figure 7, the comparison of the data by Timrot et al.[30] with our values is shown. Up to densities of about 1 mol·L^{-1}, our values agree with the data by Timrot et al., determined in the all-of-quartz oscillating-disk viscometer with an uncertainty of ±0.7%, within ±0.4%. With increasing density, the data by Timrot et al. show a tendency to

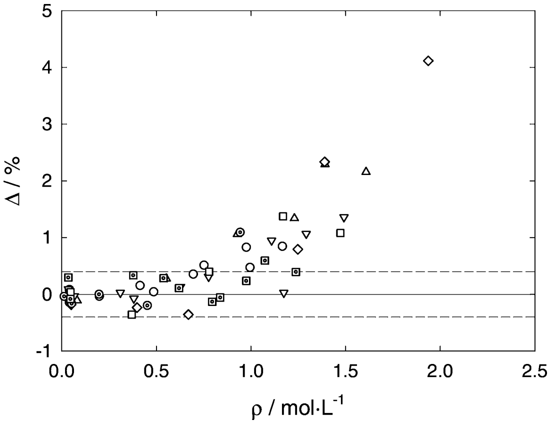

Figure 7. Comparison of experimental viscosity data by Timrot et al.[30] at higher densities with the results of this paper according to eq 1 with the coefficients for the highest order in δ from Table 2. Deviations [$\triangle = 100(\eta_{\text{lit}} - \eta_{\text{present}})/\eta_{\text{present}}$] as a function of density ρ: ○, 300 K; △, 316 K; ◇, 321 K; ▽, 333.15 K; □, 350 K; ⊙, 375 K; ⊡, 400 K.

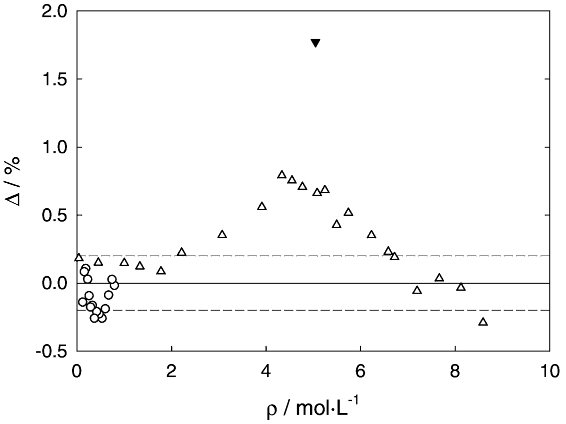

Figure 8. Comparison of experimental viscosity data from the literature at higher densities with the results of the present work according to eq 1 with the coefficients for the highest order in δ from Table 2. Deviations [$\triangle = 100(\eta_{\text{lit}} - \eta_{\text{present}})/\eta_{\text{present}}$] as a function of density ρ: ○, Hurly et al.[33] at 298.15 K; △, Hoogland et al.[31] at 333.15 K; ▼, Hoogland et al.[46] at 321 K.

higher values, up to 4% beyond the mutual uncertainties. Nevertheless, these data are probably better suitable to be used for a sound data correlation, but they are limited to comparably small densities.

As illustrated in Figure 8, the experimental data by Hurly et al.[33] at 298.15 K restricted to molar densities of 0.8 mol·L^{-1} agree with our values within ±0.3%. This corresponds to the uncertainty of 0.3% estimated by Hurly et al. for their data determined with the acoustic viscometer. Furthermore, the data by Hoogland et al.[31] for the 333.15 K isotherm show differences beyond ±0.3% only for densities of $3 < \rho/\text{mol·L}^{-1} < 6.5$. This is practically the same density range for which, as we have discussed in the last section, the description with the series expansion that is sixth order in δ results in deviations greater than ±(0.1 to 0.2)%. Hoogland et al. estimated the uncertainty of their data to be ±0.1% when described with a series expansion that is seventh order in reduced density. The largest deviation of +0.8% at about 4 mol·L^{-1} exceeds the mutual uncertainties dominated by our uncertainty of ±0.4% at higher densities. Even if a small difference of 0.1% in the densities, due to the compressibility data of Biswas et al.[50] and employed by Hoogland et al., is taken into account, it could be that our values areslightly too small. This is in agreement with the results for the 321 K isotherm but with a weakened tendency. However, the data by Hoogland et al. could also be influenced by very small uncertainties of the pressures needed for the evaluation of their viscosity measurements. The mutual good agreement between the data by Hurly et al.,[33] Hoogland et al.,[31] and this paper predetermines them to be used as reference values for a viscosity surface correlation.

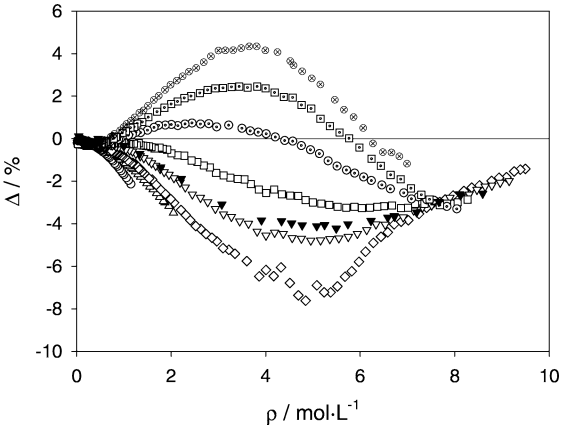

Figure 9. Comparison of the experimental viscosity data of this work at different temperatures and of Hoogland et al.[31] with the viscosity surface correlation by Altunin.[5] Deviations [$\triangle = 100(\eta_{\text{expt}} - \eta_{\text{cor}})/\eta_{\text{cor}}$] as a function of density ρ: ○, 300 K; △, 316 K; ◇, 321 K; ▽, 333.15 K; □, 350 K; ⊙, 375 K; ⊡, 400 K; ⊗, 425 K; ▼, Hoogland et al.[31] at 333.15 K.

In addition, Figure 8 shows one of the viscosity values measured by Hoogland and Trappeniers[46] with their constant-volume capillary viscometer along the critical isochore. This experimental point recalculated to 321 K is increased by +1.8% compared with our fit of the 321 K isotherm in which all of the experimental points in the near-critical region were excluded. Generally, the relative critical enhancement of the viscosity is estimated to be +1% for the near-critical density when the temperature is about 1% distant from the critical temperature.[51] Subtracting the effect of the critical enhancement gives the same deviation of about +0.8% as for the 333.15 K isotherm by Hoogland et al.[31]

As mentioned in the Introduction, Altunin[5] reported a representation for the complete viscosity surface of the fluid based essentially on three experimental data sets. Apart from the experimental results by Ulybin and Makarushkin[52] in the liquid region, only the experimental data by Timrot et al.[30] and by Grigoriev et al.[47] were included. Figure 9 illustrates that there are large differences between the correlation by Altunin and the data by Hoogland et al.[31] as well as our values. A closer look shows that our values change in a systematic manner with temperature but not in accordance with the data by Grigoriev et al. (Figure 6). The equation of state used by Altunin could have additionally influenced the differences observed.

Recently, Hafer[48] proposed another viscosity surface correlation for sulfur hexafluoride using results of own measurements in the liquid phase and for a supercritical isotherm at 325 K as well as the data by Ulybin and Makarushkin[52] in the liquid phase. Hafer performed his measurements (see also Hafer and Laesecke[49]) in the temperature range from (225 to 325) K with pressures up to 35 MPa using a torsional crystal viscometer both in the forced-resonance and in the free-decay modes. The results of both measurement modes were found to be consistent up to a (viscosity × density) of 0.020 (Pa·s) (kg·m^{-3}), whereas at higher values of the product the free-decay

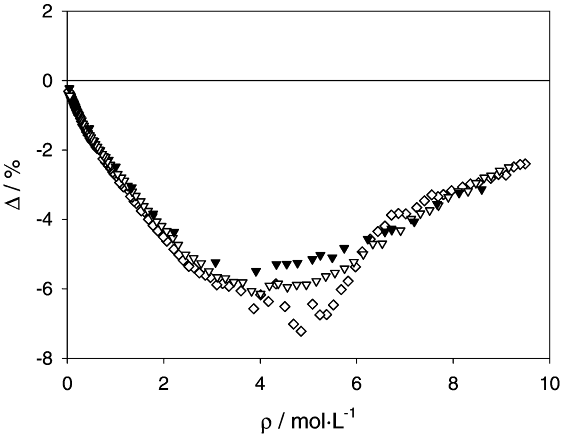

Figure 10. Comparison of the experimental viscosity data of this work at different temperatures and of Hoogland et al.[31] with the viscosity surface correlation by Hafer.[48] Deviations [$\Delta = 100(\eta_{\mathrm{expt}} - \eta_{\mathrm{cor}})/\eta_{\mathrm{cor}}$] as a function of density ρ: ◇, 321 K; ▽, 333.15 K; ▼, Hoogland et al.[31] at 333.15 K.

mode leads to data systematically lower by >6%. The uncertainty of the data resulting for both modes was estimated to be ±3%. Nevertheless, Hafer based his correlation only on the forced-mode data. The deviations of the experimental values of this paper at (321 and 333.15) K and of Hoogland et al.[31] from the correlation by Hafer are shown in Figure 10. The data by Hoogland et al. as well as the values in this paper are lower than the correlation, with deviations up to 6% near the critical density. Hence, they deviate also by the same order from the experimental data by Hafer, which is the basis of the correlation in this thermodynamic range.

A comparison with the deviations from the correlation by Altunin[5] in Figure 9 shows analogous behavior for these isotherms, but we are convinced that the data by Hoogland et al.[31] and that in this paper are the most reliable. Therefore, Figures 9 and 10 make evident that there is a real need to improve the viscosity surface correlations available.

Conclusions

The measurements in this paper performed on sulfur hexafluoride with a vibrating-wire viscometer are generally characterized by a reproducibility of ±(0.05 to 0.1)% and an uncertainty of ±(0.25 to 0.4)%. There is obviously a distinct increase in the uncertainty near the critical region, possibly (1 to 2)%. This is probably due to small uncertainties of the measured pressures and temperatures, which lead to high uncertainties in the calculated densities because of the strong compressibility in this thermodynamic region. The experimental equipment and the evaluation procedure for the viscosity measurements will be improved by a simultaneous density measurement using the single-sinker method based on the buoyancy principle.[53]

The viscosity surface correlations reported by Altunin[5] and by Hafer[48] are not sufficient for a reasonable representation of the viscosity of sulfur hexafluoride and have to be improved using a suitable database. With regard to such a database, the data in this paper are the most comprehensive, highly accurate values in the gaseous phase. The agreement with the data by Hoogland et al.[31] within ±0.3% apart from the near-critical region demonstrates that the data sets of both groups should be included in the database for the development of an improved viscosity surface correlation. The data by Timrot et al.[30] up to 1 mol·L^{-1} and by Hurly et al.[33] are also suitable for the database.

The viscosity surface correlation does not need to take into account a logarithmic term that is quadratic in density, even if the experimental data are of very high accuracy.

Literature Cited

(1) Hurly, J. J.; Defibaugh, D. R.; Moldover, M. R. Thermodynamic Properties of Sulfur Hexafloride. *Int. J. Thermophys.* **2000**, *21*, 739−765.

(2) Wagner, W.; Kurzeja, N. Private communication, 2004.

(3) Trengove, R. D.; Wakeham, W. A. The Viscosity of Carbon Dioxide, Methane, and Sulfur Hexafluoride in the Limit of Zero Density. *J. Phys. Chem. Ref. Data* **1987**, *16*, 175−187.

(4) Strehlow, T.; Vogel, E. Temperature Dependence and Initial Density Dependence of the Viscosity of Sulphur Hexafluoride. *Physica A* **1989**, *161*, 101−117.

(5) Altunin, V. V. Equation for the Viscosity of Sulfur Hexafluoride for a Broad Range of Temperatures and Pressures. *Tr. Mosk. Energ. Inst.* **1984**, *622*, 12−18.

(6) Boushehri, A.; Bzowski, J.; Kestin, J.; Mason, E. A. Equilibrium and Transport Properties of Eleven Polyatomic Gases at Low Density. *J. Phys. Chem. Ref. Data* **1987**, *16*, 445−466.

(7) Aziz, R. A.; Slaman, M. J.; Taylor, W. L.; Hurly, J. J. An Improved Intermolecular Potential for Sulfur Hexafluoride. *J. Chem. Phys.* **1991**, *94*, 1034−1038.

(8) Meinander, N. An Anisotropic Intermolecular Potential for Sulfur Hexafluoride Based on the Collision Induced Light Scattering, Viscosity, and Virial Coefficient Data. *J. Chem. Phys.* **1993**, *99*, 8654−8667.

(9) Stefanov, B.; Zarkova, L.; Fokin, L. R.; Lyusternik, V. E.; Altunin, V. V.; Tozkii, E. E. Thermophysical Properties of Gaseous Sulphur Hexafluoride in the Range 220−1000 K: 43 Experiments Described by a Unique Intermoleculer Potential. *High Temp. − High Pressures* **1991**, *23*, 461−471.

(10) Stefanov, B.; Zarkova, L. The Model of Vibrationally Excited States of Molecules as a Tool for Calculating Thermodynamic and Transport Properties of Molecular Gases: SF_6 as an Example. *High Temp. − High Pressures* **1993**, *25*, 487−490.

(11) Zarkova, L.; Hohm, U. *pVT*-Second Virial Coefficients $B(T)$, Viscosity $\eta(T)$, and Self-Diffusion $\rho D(T)$ of the Gases: BF_3, CF_4, SiF_4, SF_6, MoF_6, WF_6, UF_6, $C(CH_3)_4$, and $Si(CH_3)_4$ Determined by Means of an Isotropic Temperature-Dependent Potential. *J. Phys. Chem. Ref. Data* **2002**, *31*, 183−216.

(12) Wilhelm, J.; Vogel, E.; Lehmann, J. K.; Wakeham, W. A. Vibrating-Wire Viscometer for Dilute and Dense Gases. *Int. J. Thermophys.* **1998**, *19*, 391−401.

(13) Wilhelm, J.; Vogel, E. Viscosity Measurements on Gaseous Argon, Krypton, and Propane. *Int. J. Thermophys.* **2000**, *21*, 301−318.

(14) Wilhelm, J.; Vogel, E. Viscosity Measurements on Gaseous Propane. *J. Chem. Eng. Data* **2001**, *46*, 1467−1471.

(15) Vogel, E.; Wilhelm, J.; Küchenmeister, C.; Jaeschke, M. High-Precision Viscosity Measurements on Methane. *High Temp. − High Pressures* **2000**, *32*, 73−81.

(16) Schley, P.; Jaeschke, M.; Küchenmeister, C.; Vogel, E. Viscosity Measurements and Predictions for Natural Gas. *Int. J. Thermophys.* **2004**, *25*, 1623−1652.

(17) Vogel, E.; Küchenmeister, C.; Jaeschke, M. Experience of Measurements with a Vibrating-Wire Viscometer on Natural Gases. *Int. J. Thermophys.* **2004**, *25*, 1653−1665.

(18) Retsina, T.; Richardson, S. M.; Wakeham, W. A. The Theory of a Vibrating-Rod Viscometer. *Appl. Sci. Res.* **1987**, *43*, 325−346.

(19) Kestin, J.; Leidenfrost, W. An Absolute Determination of the Viscosity of Eleven Gases over a Range of Pressures. *Physica* **1959**, *25*, 1033−1063.

(20) Sengers, J. V. Density Expansion of the Viscosity of a Moderately Dense Gas. *Phys. Rev. Lett.* **1965**, *15*, 515−517.

(21) Kamgar-Parsi, B.; Sengers, J. V. Logarithmic Density Dependence of the Transport Properties of Gases. *Phys. Rev. Lett.* **1983**, *51*, 2163−2166.

(22) Kestin, J.; Paykoc, E.; Sengers, J. V. Density Expansion for Viscosity in Gases. *Physica* **1971**, *54*, 1−19.

(23) Van den Berg, H. R. Precisiemetingen aan de Viscositeitscoefficient van Krypton en de logarithmische Term in de Dichtheidsontwikkeling. Ph.D. Thesis, University of Amsterdam, 1979.

(24) Cohen, E. G. D. The Kinetic Theory of Moderately Dense Gases. In *Transport Phenomena in Fluids*; Hanley, H. J. M., Ed.; Marcel Dekker: New York, 1969; Chapter 7, pp 157−207.

(25) Earwicker, G. A.; Fear, E. J. P. Viscosity of Gaseous Sulfur Hexafluoride. *Chem. Ind.* **1954**, 903−904.

(26) McCoubrey, J. C.; Singh, N. M. Intermolecular Forces in Quasi-Spherical Molecules *Trans. Faraday Soc.* **1957**, *53*, 877−883.

(27) Ellis, C. P.; Raw, C. J. G. High-Temperature Gas Viscosities. II. Nitrogen, Nitric Oxide, Boron Trifluoride, Silicon Tetrafluoride, and Sulfur Hexafluoride. *J. Chem. Phys.* **1959**, *30*, 574−576.

(28) Raw, C. J. G.; Tang, H. Viscosity and Diffusion Coefficients of Gaseous $SF_6 + CF_4$ Mixtures. *J. Chem. Phys.* **1963**, *39*, 2616−2618.

(29) Kestin, J.; Ro, S. T.; Wakeham, W. A. Reference Values of the Viscosity of Twelve Gases at 25 °C. *Trans. Faraday Soc.* **1971**, *67*, 2308−2313.

(30) Timrot, D. L.; Serednitskaya, M. A.; Traktueva, S. A. Viscosity of Sulfur Hexafluoride Studied by the Vibrating Disk Method. *Teplofiz. Vys. Temp.* **1975**, *13*, 1112−1116.

(31) Hoogland, J. H. B.; van den Berg, H. R.; Trappeniers, N. J. Measurements of the Viscosity of Sulfur Hexafluoride up to 100 bar by a Capillary-Flow Viscometer. *Physica A* **1985**, *134*, 169−192.

(32) Berg, R. F. Private communication, 2004.

(33) Hurly, J. J.; Gillis, K. A.; Mehl, J. B.; Moldover, M. R. The Viscosity of Seven Gases Measured with a Greenspan Viscometer. *Int. J. Thermophys.* **2003**, *24*, 1441−1474.

(34) Hellemans, J. M.; Kestin, J.; Ro, S. T. Viscosity of Methane, Carbon Tetrafluoride, and Sulfur Hexafluoride over a Range of Temperatures. *Physica* **1973**, *65*, 376−380.

(35) Kestin, J.; Khalifa, H. E.; Wakeham, W. A. Viscosity of Multicomponent Mixtures of Four Complex Gases. *J. Chem. Phys.* **1976**, *65*, 5186−5188.

(36) Kestin, J.; Khalifa, H. E.; Ro, S. T.; Wakeham, W. A. The Viscosity and Diffusion Coefficients of Eighteen Binary Gaseous Systems. *Physica A* **1977**, *88*, 242−260.

(37) Kestin, J.; Khalifa, H. E.; Wakeham, W. A. The Viscosity of Gaseous Mixtures Containing Krypton. *J. Chem. Phys.* **1977**, *67*, 4254−4259.

(38) Abe, Y.; Kestin, J.; Khalifa, H. E.; Wakeham, W. A. The Viscosity and Diffusion Coefficients of the Mixtures of Light Hydrocarbons with Other Polyatomic Gases. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 271−276.

(39) Vogel, E.; Küchenmeister, C.; Bich, E.; Laesecke, A. Reference Correlation of the Viscosity of Propane. *J. Phys. Chem. Ref. Data* **1998**, *27*, 947−970.

(40) Dawe, R. A.; Maitland, G. C.; Rigby, M.; Smith, E. B. High-Temperature Viscosities and Intermolecular Forces of Quasi-Spherical Molecules. *Trans. Faraday Soc.* **1970**, *66*, 1955−1965.

(41) Harris, E. J.; Hope, G. C.; Gough, D. W.; Smith, E. B. Viscosity of Gaseous Carbon Dioxide, Sulphur Hexafluoride and Nitrous Oxide at Low Temperatures. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 892−897.

(42) Ueda, K.; Kigoshi, K. Viscosity of the Gaseous Hexafluorides of Sulfur, Selenium, and Tellurium. *J. Inorg. Nucl. Chem.* **1974**, *36*, 989−992.

(43) Tanaka, Y.; Nakajima, M.; Kubota, H.; Makita, T. Viscosity of $SF_6 + N_2$ and SF_6 + He Gaseous Mixtures. *J. Chem. Eng. Jpn.* **1980**, *13*, 155−159.

(44) Lukin, V. I.; Ivakin, B. A.; Suetin, P. E. Viscosity of Some Gases Measured by an Unsteady Flow Method. *Zh. Tekh. Fiz.* **1981**, *51*, 860−862.

(45) Lukin, V. I.; Ivakin, B. A.; Suetin, P. E. Temperature Dependence of Coefficients of Viscosity of Some Gases. *Zh. Tekh. Fiz.* **1983**, *53*, 931−932.

(46) Hoogland, J. H. B.; Trappeniers, N. J. The Coefficient of the Viscosity of Sulfur Hexafluoride along the Critical Isochore. *Proc. Symp. Thermophys. Props.* **1982**, *8*, 440−442.

(47) Grigoriev, B. A.; Keramidi, A. S.; Grachev, V. K.; Rastorguev, Yu. L. Experimental Study of Sulfur Hexafluoride Viscosity. *Teploenergetika* **1977**, *9*, 85−87.

(48) Hafer, R. F. Torsional Crystal Viscometry: Wide Ranging Resonance Measurements and Feasibility Study of Transient-Decay Measurements. MSc Thesis, Department of Chemical Engineering, University of Colorado, 1999.

(49) Hafer, R. F.; Laesecke, A. Extension of the Torsional Crystal Viscometer to Measurements in the Time Domain. *Meas. Sci. Technol.* **2003**, *14*, 663−673.

(50) Biswas, S. N.; Trappeniers, N. J.; Hoogland, J. H. B. *PVT* Properties of Sulfur Hexafluoride in the Gas-Liquid Critical Region. *Physica A* **1984**, *126*, 384−415.

(51) Vesovic, V.; Millat, J. Polyatomic Fluids - Ethane. In *Transport Properties of Fluids: Their Correlation, Prediction, and Estimation*; Millat, J., Dymond, J. H., Nieto de Castro, C., Eds.; Cambridge University Press: Cambridge, U.K., 1996; Chapter 14.3, pp 348−363.

(52) Ulybin, S. A.; Makarushkin, V. I. Viscosity of Sulfur Hexafluoride at Temperatures of 230-800 K and Pressures up to 50 MPa. *Teplofiz. Vys. Temp.* **1977**, *15*, 1195−1201.

(53) Wagner, W.; Brachthäuser, K.; Kleinrahm, R.; Lösch, H. W. A New Accurate Single-Sinker Densitometer for Temperatures from 233 to 523 K at Pressures up to 30 MPa. *Int. J. Thermophys.* **1995**, *16*, 399−411.

Received for review November 5, 2004. Accepted January 18, 2005. We are grateful to Deutsche Forschungsgemeinschaft (Germany) for financial support.

JE049612F