

## Viscosity Measurements on Gaseous Ethane

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A vibrating-wire viscometer of very high precision was used to measure the viscosity of gaseous ethane. The experimental data were taken at subcritical temperatures of (290 and 300) K up to 88 % of the saturated vapor pressure and at supercritical temperatures of (310, 320, 340, 370, 400, and 430) K at pressures up to a maximum of 30 MPa. The measuring values were evaluated using an equation of state by Bücker and Wagner. The reproducibility is  $\pm$  (0.05 to 0.1) %, whereas the total uncertainty is estimated to be  $\pm$  (0.25 to 0.4) % with an increase of (1 to 2) % close to the critical point. The viscosity values of the isotherms were correlated as a function of reduced density using a power series expansion. A comparison with correlations from the literature shows deviations up to about 5 % in the near critical region and up to 2 % at higher densities and temperatures. On the basis of a comparison with direct experimental data from the literature, it is concluded that the new values are the most reliable for the improvement of the viscosity surface correlation of ethane.

### Introduction

Ethane is of large industrial importance as a major component of natural gas, so that its thermodynamic properties have been investigated rather frequently. The most recent equation of state for thermodynamic properties of ethane was reported by Bücker and Wagner.<sup>1</sup> Values of the transport properties have not been determined with the same high accuracy as the thermodynamic data. Friend et al.<sup>2</sup> as well as Hendl et al.<sup>3</sup> and Vesovic et al.<sup>4</sup> presented complete transport property surface correlations of the fluid, all suffering from the limited number of experimental data and their uncertainties. It is obvious that new high-precision values are needed to improve the correlations based on a critical evaluation of all available data. Furthermore, transport properties of ethane cannot be calculated in a reasonable manner because there do not exist appropriate intermolecular hypersurfaces as well as the corresponding kinetic theory, both at low and at high densities, for complex molecules such as ethane.

Some years ago Wilhelm et al.<sup>5</sup> constructed a vibrating-wire viscometer and carried out high-precision measurements on argon, krypton, and propane between (298 and 423) K up to a maximum pressure of 20 MPa.<sup>6,7</sup> Very recently, measurements on sulfur hexafluoride were performed with the same instrument at two subcritical temperatures of (300 and 316) K in the vapor phase region and at six supercritical temperatures between (321 and 425) K at pressures up to 20 MPa.<sup>8</sup>

With regard to the needs of the gas industry, a special measuring program was started to determine the viscosity of natural gas components and of natural gas mixtures in the thermodynamic range of interest. First, the viscosity of methane<sup>9,10</sup> and of two natural gases<sup>10,11</sup> was measured. Here the program has been extended to ethane for which eight isothermal series of measurements, two at subcritical and six at supercritical temperatures, were carried out. The results should contribute to a more

accurate database for the viscosity surface of this industrially important substance.

### Experimental Section

Wilhelm et al.<sup>5</sup> and Wilhelm and Vogel<sup>6</sup> have described the instrument in detail. Hence, only some essential features are necessary to be mentioned. The wire with a length of 90 mm and a diameter of about 25  $\mu\text{m}$  is symmetrically arranged in a magnetic field so that even harmonics cannot be initiated. Furthermore, the ratio between the lengths of wire and the field has been chosen to be 1.5 in order to suppress the third harmonic mode of the oscillation. The wire is made of Chromel to avoid the influence of a rough surface in the case of measurements on dilute and even on dense gases. For measurements on liquids, tungsten is preferentially used due to its excellent mechanical properties, although its surface is very rough.

The oscillation, following a sinusoidal voltage pulse with a frequency close to the resonant frequency of the wire, is detected by amplifying the induced voltage and measuring it as a function of time. To improve the signal-to-noise ratio a hundred runs of oscillations are measured and averaged to one oscillation curve. The parameters of the oscillation, the logarithmic decrement ( $\Delta$ ) and the frequency ( $\omega$ ), are deduced from averaged oscillation curves starting with different displacements ( $y_{\text{max}}$ ). The correct values of  $\Delta$  and  $\omega$  are obtained by extrapolation of their values as a function of the square of the relative initial amplitude  $\epsilon = y_{\text{max}}/R$  to  $\epsilon^2 \rightarrow 0$ . This procedure is necessary since comparably large displacements ( $y$ ) related to the wire radius ( $R$ ) are needed for reasonably large measuring signals, whereas the measuring theory requires small displacements ( $y$ ) in the order of 1 % of the wire radius ( $R$ ).

The viscometer cell is placed in a pressure vessel surrounded by a heat-pipe thermostat. The pressure is measured using four pressure transmitters supplied by Digiquartz. They are characterized by uncertainties of  $\pm$  0.01 % of their full scale working ranges of (0.69, 2.76, 13.8, and 41.4) MPa. A premium ITS-90 thermometer and a 6<sup>1</sup>/<sub>2</sub> digit multimeter are applied to measure the temperature with an uncertainty of  $\pm$  0.015 K.

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The viscosity ( $\eta$ ) results from the deduced values of  $\Delta$  and  $\omega$  using the working equations of the theory for the vibrating-wire viscometer.<sup>12</sup> Here it is provided that the density ( $\rho$ ) of the fluid, the density ( $\rho_s$ ) and the radius ( $R$ ) of the wire, and the parameters of the oscillation in vacuo ( $\Delta_0$  and  $\omega_0$ ) are known. It is to be considered that the wire radius ( $R$ ) cannot be obtained accurately by direct measurements, so that it has to be determined on the basis of measurements of a gas with a viscosity value reliably known for a certain thermodynamic state. For that purpose, measurements on argon at room temperature were performed, and a value of  $R = (12.770 \pm 0.005) \mu\text{m}$  resulted, using reference values by Kestin and Leidenfrost<sup>13</sup> and assuming the density of the wire material Chromel to be  $8500 \text{ kg}\cdot\text{m}^{-3}$  as given by the supplier.

## Measurements and Results

The subcritical isotherms of the measurements on gaseous ethane at (290 and 300) K extended over ranges up to 88 % of the saturated vapor pressure, whereas the supercritical isotherms at (310, 320, 340, 370, 400, and 430) K were performed up to 30 MPa. The purity of ethane supplied by Messer Griesheim (Germany) has been certified to be 99.95 %. The densities ( $\rho$ ) needed for the determination of the viscosity were derived from the measured pressures ( $p$ ) and temperatures ( $T$ ) with the equation of state by Bückner and Wagner.<sup>1</sup>

The isothermal series of measurements include about 100 data points. Although the individual points could not be measured exactly at the nominal temperatures of the isotherms, the experimental data could be adjusted to the nominal temperature. For that purpose, a Taylor expansion restricted to a second power in temperature was used since the deviations of the experiments from the nominal temperatures were kept within  $\pm 0.1$  K. Here the densities directly deduced from the experiments and those for the isotherms are the same. The pressures at the nominal temperatures of the isotherms were subsequently redetermined from the densities. The results for all series of measurements are summarized in Table 1. Only the pressures, densities, and viscosities are given in the table with regard to the large number of experimental points. The measurements on propane,<sup>7</sup> sulfur hexafluoride,<sup>8</sup> and methane<sup>10</sup> have shown that experimental values at pressures below 0.1 MPa could be influenced by the slip effect. For the measurements on ethane, the minimum pressures for the isotherms do not fall below 0.07 MPa. Surprisingly, a critical inspection of the experimental values showed that no one was identified to be influenced by slip.

In general, the measurements are characterized by a reproducibility of less than  $\pm 0.05$  %. In addition, errors arising from the uncertainty of the calibration values<sup>13</sup> ( $\pm 0.1$  %) and the density calculation have to be taken into account. The uncertainty of the density has two impacts on the viscosity. The gas density is used in the working equations to deduce the viscosity from the measured values ( $\Delta$  and  $\omega$ ) and represents simultaneously a variable of the viscosity. In most cases, an uncertainty of  $\pm 0.2$  % in the density values causes a change of  $\pm 0.1$  % in the viscosity only. Hence, the total uncertainties of the viscosity are conservatively assessed to amount to  $\pm 0.25$  % for  $\rho < 4 \text{ mol}\cdot\text{dm}^{-3}$  and  $\pm 0.4$  % for higher densities. But the uncertainty is distinctly enlarged when the critical region is approached. This is demonstrated in the next section for the 310 K isotherm, particularly for the reduced density range  $0.7 \leq \delta \leq 1.3$ .

## Analysis

For the evaluation of the isotherms, the viscosity values were correlated as a function of the reduced density ( $\delta$ ) by means of a power series representation (eq 1) restricted to the sixth or a lower power depending on the density range included:

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

$$\delta = \frac{\rho}{\rho_{c,C_2H_6}} \quad \rho_{c,C_2H_6} = 6.8569 \text{ mol}\cdot\text{dm}^{-3}$$

$$\tau = \frac{T}{T_{c,C_2H_6}} \quad T_{c,C_2H_6} = 305.322 \text{ K}$$

The values of the critical constants correspond to those given by Bückner and Wagner.<sup>1</sup> Weighting factors of  $(100/\eta)^2$  were used in the multiple linear least-squares regression to minimize the relative deviations. The weighted standard deviation ( $\sigma$ ) was used as criterion for the description of the considered isotherm and was related to the maximum density of the experimental points included in a fit by means of eq 1.

Figure 1 illustrates for the 300 K isotherm, which includes experimental values up to  $2.56 \text{ mol}\cdot\text{dm}^{-3}$ , that a series expansion with a fourth order in the reduced density ( $\delta$ ) is suitable for an appropriate representation. It is evident from Figure 2 that a series expansion of the sixth order in  $\delta$  is needed for the 320 K isotherm to describe all experimental points up to molar densities of  $13.6 \text{ mol}\cdot\text{dm}^{-3}$ . In addition, this figure shows a slightly increasing standard deviation ( $\sigma$ ) in the density range  $4.5 < \rho/\text{mol}\cdot\text{dm}^{-3} < 9$ . With regard to the problems expected for the determination of the density from measured temperatures and pressures close to the critical region, we have had a closer look at the 310 K isotherm nearest to the critical temperature. In Figure 3, the deviations of the experimental points from a fit with a series expansion of the sixth order in  $\delta$  are presented. It is obvious that comparably large relative deviations [ $\Delta = 100 \cdot (\eta_{\text{exp}} - \eta_{\text{fit}})/\eta_{\text{fit}}$ ] of  $-0.3$  % to  $+0.6$  % appear in the density range  $5 < \rho/\text{mol}\cdot\text{dm}^{-3} < 9$ . As a consequence, the experimental data from this density range were excluded in a new fit. As indicated additionally in Figure 3, the deviations for those points included in the fit were within  $\pm 0.1$  %, whereas the disqualified ones deviate systematically up to  $+0.8$  %. These data are marked in Table 1. The reason for the increases in the reproducibility up to  $\pm 0.1$  % and in the uncertainty up to  $\pm 1$  % could be that close to the critical point small uncertainties of the measured pressures and temperatures result in high uncertainties for the derived densities due to the strong compressibility in this thermodynamic region. The critical enhancement of the viscosity amounts to approximately 1 % in the same thermodynamic region for temperatures within 1 % of the critical one. This can be derived from Figure 2 of the paper by Hendl et al.<sup>3</sup>, in which the experimental data by Iwasaki and Takahashi<sup>14</sup> were used to demonstrate the critical enhancement of viscosity of ethane. This corresponds to the increase of  $+0.8$  % for the 310 K isotherm of ethane as mentioned above. But our measurements on sulfur hexafluoride<sup>8</sup> showed in the corresponding thermodynamic range for the 321 K isotherm (see Figure 3 of that paper) negative deviations up to  $-1.7$  %. Hence, it is not possible to clarify whether the small uncertainties of the measured pressures and temperatures or the critical enhancement are responsible for the inappropriate description of these near critical isotherms. Although most authors claim a comparably low uncertainty, even in the near critical region, it has to

Table 1. Experimental Viscosity Values of Ethane along Isotherms

$p$	$\rho$	$\eta$	$p$	$\rho$	$\eta$	$p$	$\rho$	$\eta$	$p$	$\rho$	$\eta$	$p$	$\rho$	$\eta$
MPa	mol·dm <sup>-3</sup>	μPa·s	MPa	mol·dm <sup>-3</sup>	μPa·s	MPa	mol·dm <sup>-3</sup>	μPa·s	MPa	mol·dm <sup>-3</sup>	μPa·s	MPa	mol·dm <sup>-3</sup>	μPa·s
$T = 290$ K														
2.9160	1.7553	10.021	2.2275	1.1787	9.547	1.4381	0.68496	9.239	0.77523	0.34431	9.084	0.32737	0.13956	9.023
2.8901	1.7294	10.000	2.1394	1.1170	9.502	1.3501	0.63660	9.213	0.71098	0.31383	9.075	0.30059	0.12784	9.019
2.8536	1.6937	9.968	2.0806	1.0769	9.475	1.2593	0.58785	9.188	0.67153	0.29532	9.068	0.27101	0.11497	9.018
2.7954	1.6384	9.918	2.0267	1.0409	9.451	1.2166	0.56527	9.177	0.63689	0.27918	9.063	0.24646	0.10434	9.015
2.7478	1.5946	9.879	1.9468	0.98873	9.416	1.1817	0.54698	9.169	0.59519	0.25989	9.059	0.22558	0.095324	9.013
2.6751	1.5299	9.822	1.8845	0.94902	9.391	1.1233	0.51671	9.155	0.55620	0.24200	9.053	0.20262	0.085457	9.013
2.6026	1.4679	9.773	1.8160	0.90618	9.365	1.0644	0.48665	9.142	0.50887	0.22045	9.048	0.17698	0.074482	9.009
2.5327	1.4103	9.725	1.7168	0.84579	9.326	1.0095	0.45891	9.131	0.47696	0.20603	9.042	0.14827	0.062247	9.006
2.4754	1.3644	9.690	1.6673	0.81632	9.308	0.95842	0.43344	9.120	0.43794	0.18852	9.037	0.12424	0.052057	9.001
2.4387	1.3357	9.664	1.6153	0.78576	9.293	0.91328	0.41115	9.109	0.41283	0.17732	9.032	0.10308	0.043114	8.998
2.3473	1.2660	9.611	1.5595	0.75350	9.275	0.88203	0.39586	9.103	0.37873	0.16218	9.029	0.079597	0.033227	8.994
2.2799	1.2163	9.574	1.4848	0.71110	9.250	0.82527	0.36832	9.095	0.35388	0.15121	9.026			
$T = 300$ K														
3.8380	2.5581	11.300	2.8537	1.5387	10.191	1.7609	0.82430	9.646	0.86908	0.37334	9.413	0.33453	0.13754	9.333
3.8007	2.5045	11.232	2.7457	1.4560	10.119	1.6536	0.76531	9.611	0.81314	0.34763	9.405	0.30563	0.12538	9.329
3.7600	2.4483	11.166	2.6881	1.4132	10.080	1.6107	0.74213	9.599	0.77872	0.33194	9.396	0.27546	0.11274	9.324
3.6927	2.3599	11.058	2.6062	1.3540	10.032	1.5510	0.71023	9.580	0.72832	0.30914	9.387	0.25424	0.10388	9.323
3.6199	2.2700	10.950	2.5584	1.3202	10.004	1.5149	0.69118	9.568	0.68378	0.28915	9.381	0.22420	0.091403	9.323
3.5352	2.1715	10.832	2.4554	1.2493	9.947	1.4464	0.65543	9.548	0.64995	0.27408	9.377	0.20362	0.082883	9.315
3.4836	2.1144	10.772	2.3917	1.2066	9.914	1.3646	0.61342	9.525	0.61884	0.26029	9.372	0.17840	0.072477	9.312
3.4042	2.0303	10.681	2.3338	1.1685	9.884	1.3213	0.59147	9.516	0.57991	0.24314	9.365	0.15172	0.061515	9.312
3.3491	1.9744	10.616	2.2440	1.1108	9.843	1.2515	0.55652	9.496	0.54578	0.22820	9.362	0.12556	0.050810	9.310
3.2674	1.8948	10.532	2.1304	1.0400	9.791	1.1600	0.51146	9.474	0.50729	0.21144	9.355	0.10260	0.041445	9.304
3.2138	1.8445	10.485	2.0827	1.0110	9.771	1.1164	0.49027	9.464	0.48195	0.20048	9.352	0.071393	0.028773	9.301
3.1318	1.7702	10.408	2.0056	0.96481	9.738	1.0646	0.46533	9.454	0.44723	0.18552	9.348			
3.0545	1.7029	10.344	1.9103	0.90901	9.699	1.0135	0.44095	9.444	0.41992	0.17381	9.344			
2.9866	1.6458	10.289	1.8713	0.88663	9.688	0.97432	0.42243	9.434	0.38848	0.16040	9.340			
2.9049	1.5792	10.227	1.8292	0.86262	9.672	0.91125	0.39290	9.420	0.35806	0.14749	9.337			
$T = 310$ K														
24.935	13.999	66.613	5.4932	8.2397	26.010 <sup>a</sup>	4.5963	3.1838	12.557	2.1580	0.99677	10.087	0.67029	0.27252	9.678
22.390	13.768	63.843	5.4602	8.0119	25.147 <sup>a</sup>	4.4949	3.0183	12.316	2.0783	0.95234	10.055	0.62338	0.25258	9.675
19.609	13.480	60.659	5.4351	7.8011	24.283 <sup>a</sup>	4.3705	2.8359	12.053	1.9983	0.90854	10.026	0.58186	0.23504	9.666
18.248	13.322	58.971	5.4140	7.5902	23.525 <sup>a</sup>	4.2234	2.6429	11.787	1.9174	0.86504	9.996	0.53399	0.21496	9.659
16.313	13.073	56.464	5.3948	7.3667	22.778 <sup>a</sup>	4.0970	2.4924	11.589	1.8337	0.82078	9.967	0.49824	0.20005	9.654
14.805	12.853	54.366	5.3748	7.0997	21.827 <sup>a</sup>	3.9079	2.2882	11.337	1.7908	0.79840	9.952	0.46857	0.18774	9.648
12.756	12.503	51.214	5.3542	6.7937	20.925 <sup>a</sup>	3.7991	2.1799	11.212	1.7141	0.75889	9.928	0.43993	0.17591	9.645
11.697	12.290	49.395	5.3357	6.5090	20.022 <sup>a</sup>	3.6663	2.0555	11.063	1.6075	0.70491	9.895	0.38287	0.15247	9.635
10.618	12.040	47.357	5.3174	6.2373	19.216 <sup>a</sup>	3.5732	1.9727	10.969	1.5689	0.68562	9.884	0.35489	0.14105	9.635
9.7063	11.794	45.447	5.2969	5.9590	18.499 <sup>a</sup>	3.4456	1.8644	10.859	1.4972	0.65024	9.862	0.32847	0.13031	9.631
8.8804	11.530	43.561	5.2722	5.6700	17.793 <sup>a</sup>	3.3462	1.7839	10.776	1.4288	0.61691	9.843	0.29970	0.11866	9.629
8.2081	11.274	41.793	5.2555	5.4997	17.227 <sup>a</sup>	3.2299	1.6934	10.685	1.3576	0.58263	9.824	0.27429	0.10841	9.624
7.3832	10.879	39.220	5.2224	5.2130	16.594 <sup>a</sup>	3.1610	1.6416	10.633	1.2514	0.53231	9.798	0.24876	0.098148	9.621
6.8442	10.538	37.132	5.1955	5.0185	16.108 <sup>a</sup>	3.0156	1.5359	10.532	1.1914	0.50434	9.785	0.22630	0.089148	9.620
6.3856	10.149	34.917	5.1640	4.8232	15.640	2.9268	1.4739	10.481	1.1336	0.47763	9.770	0.20044	0.078822	9.617
6.1667	9.9052	33.593	5.1087	4.5406	15.031	2.8469	1.4195	10.431	1.0528	0.44072	9.752	0.17541	0.068858	9.609
5.9919	9.6634	32.358	5.0559	4.3191	14.569	2.7415	1.3496	10.366	0.98307	0.40929	9.738	0.14848	0.058183	9.607
5.8488	9.4150	31.134	5.0094	4.1515	14.242	2.6334	1.2802	10.306	0.92411	0.38299	9.726	0.12315	0.048173	9.605
5.7362	9.1669	29.978	4.9412	3.9386	13.843	2.5294	1.2152	10.255	0.85952	0.35445	9.711	0.099999	0.039057	9.600
5.6455	8.9108	28.898 <sup>a</sup>	4.8922	3.8039	13.594	2.4493	1.1664	10.218	0.81585	0.33533	9.706			
5.5812	8.6794	27.863 <sup>a</sup>	4.8092	3.6020	13.245	2.3483	1.1063	10.168	0.75622	0.30943	9.694			
5.5306	8.4502	26.891 <sup>a</sup>	4.7026	3.3782	12.879	2.2363	1.0412	10.120	0.71400	0.29123	9.686			
$T = 320$ K														
25.347	13.602	62.280	6.8206	8.1409	25.900	5.1502	3.3882	13.264	2.3274	1.0349	10.439	0.47780	0.24233	9.973
24.197	13.490	61.045	6.6999	7.8247	24.705	4.9715	3.1401	12.864	2.2120	0.97366	10.391	0.44882	0.22803	9.962
21.685	13.223	58.259	6.6032	7.5323	23.630	4.8026	2.9295	12.552	2.0682	0.89927	10.334	0.54411	0.21155	9.961
19.353	12.938	55.434	6.5424	7.3298	22.947	4.6798	2.7885	12.347	1.9621	0.84565	10.301	0.50918	0.19752	9.955
17.376	12.661	52.899	6.4843	7.1230	22.220	4.5065	2.6036	12.091	1.8537	0.79195	10.266	0.47780	0.18498	9.951
15.697	12.389	50.504	6.4215	6.8862	21.483	4.3264	2.4267	11.861	1.7570	0.74485	10.236	0.44882	0.17344	9.943
13.361	11.928	46.799	6.3446	6.5822	20.562	4.1742	2.2873	11.685	1.6390	0.68845	10.199	0.41210	0.15887	9.939
12.245	11.658	44.767	6.2701	6.2806	19.653	3.9955	2.1337	11.503	1.5256	0.63527	10.164	0.37795	0.14540	9.933
10.925	11.271	42.047	6.2013	6.0042	18.900	3.7112	1.9085	11.252	1.4496	0.60019	10.148	0.34557	0.13267	9.932
10.191	11.010	40.328	6.1318	5.7341	18.172	3.6280	1.8464	11.181	1.3456	0.55286	10.119	0.31302	0.11993	9.927
9.5508	10.741	38.629	6.0834	5.5542	17.701	3.4951	1.7504	11.081	1.2225	0.49782	10.088	0.27870	0.10655	9.923
9.0573	10.497	37.169	6.0174	5.3218	17.154	3.3721	1.6648	11.000	1.1259	0.45532	10.067	0.24393	0.093053	9.918
8.6069	10.234	35.683	5.9346	5.0520	16.518	3.2268	1.5673	10.897	1.0498	0.42230	10.049	0.21530	0.081988	9.914
8.2264	9.9707	34.264	5.8479	4.7953	15.926	3.0831	1.4746	10.813	0.95226	0.38046	10.030	0.18150	0.068971	9.910
7.9215	9.7203	32.950	5.7386	4.5060	15.335	2.9655	1.4010	10.746	0.89965	0.35814	10.024	0.15292	0.058010	9.904
7.5605	9.3568	31.136	5.6559	4.3091	14.933	2.8501	1.3309	10.679	0.85401	0.33892	10.014	0.11957	0.045266	9.899
7.2784	8.9953	29.498	5.5164	4.0124	14.351	2.7106	1.2486	10.612	0.78187	0.30879	9.995			
7.0846	8.6860	28.142	5.4011	3.7953	13.948	2.5942	1.1818	10.553	0.71906	0.28279	9.984			
6.9700	8.4705	27.184	5.2760	3.5824	13.578	2.4667	1.1106	10.494	0.67029	0.26276	9.979			
$T = 340$ K														
24.738	12.641	53.295	8.6446	6.9833	22.543	4.6695	2.2682	12.358	2.4990	1.0202	11.068	0.74601	0.27423	10.583
22.692														

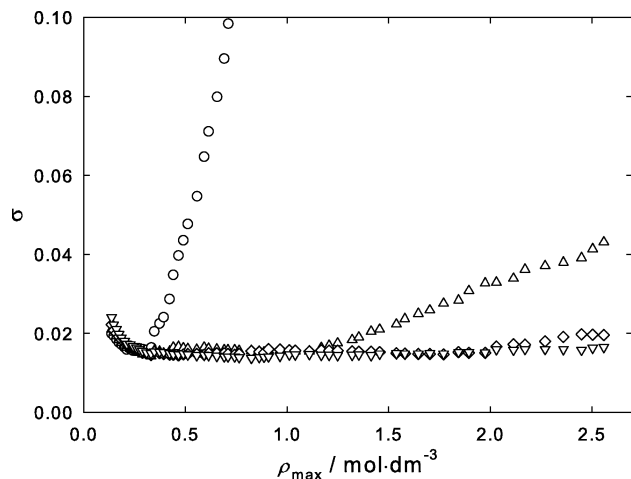
Table 1 (Continued)

$p$	$\rho$	$\eta$	$p$	$\rho$	$\eta$	$p$	$\rho$	$\eta$	$p$	$\rho$	$\eta$	$p$	$\rho$	$\eta$
MPa	mol·dm <sup>-3</sup>	μPa·s	MPa	mol·dm <sup>-3</sup>	μPa·s	MPa	mol·dm <sup>-3</sup>	μPa·s	MPa	mol·dm <sup>-3</sup>	μPa·s	MPa	mol·dm <sup>-3</sup>	μPa·s
$T = 340 \text{ K}$														
18.734	11.743	45.995	8.0816	6.1459	20.031	4.3990	2.0831	12.130	2.0760	0.82447	10.919	0.56309	0.20499	10.552
16.887	11.368	43.330	7.5834	5.3763	18.020	4.2367	1.9770	12.000	1.9563	0.77113	10.878	0.52400	0.19037	10.548
15.608	11.061	41.267	7.4038	5.1076	17.397	4.0794	1.8776	11.892	1.8418	0.72091	10.842	0.47102	0.17065	10.534
14.512	10.754	39.330	7.2218	4.8445	16.804	3.9529	1.7998	11.799	1.7295	0.67235	10.810	0.43083	0.15576	10.534
13.585	10.452	37.550	7.0409	4.5941	16.265	3.8760	1.7535	11.752	1.6160	0.62396	10.777	0.40617	0.14666	10.531
12.873	10.186	36.055	6.8484	4.3404	15.737	3.7784	1.6955	11.693	1.5500	0.59613	10.756	0.36544	0.13168	10.524
12.243	9.9155	34.616	6.6635	4.1095	15.284	3.6742	1.6349	11.631	1.4529	0.55562	10.739	0.34053	0.12254	10.519
11.651	9.6252	33.123	6.4485	3.8568	14.812	3.5644	1.5723	11.568	1.3337	0.50653	10.708	0.31773	0.11421	10.514
11.140	9.3365	31.701	6.2321	3.6183	14.377	3.4521	1.5094	11.504	1.2066	0.45495	10.676	0.28107	0.10084	10.513
10.697	9.0505	30.401	5.5568	2.9651	13.313	3.2571	1.4031	11.402	1.1335	0.42562	10.658	0.24671	0.088357	10.506
9.8547	8.3797	27.537	5.4298	2.8555	13.156	3.1313	1.3363	11.340	1.0471	0.39130	10.640	0.20375	0.072813	10.498
9.5745	8.1084	26.471	5.3123	2.7573	13.019	3.0091	1.2728	11.281	0.97806	0.36410	10.628	0.17300	0.061728	10.492
9.3227	7.8393	25.459	5.1884	2.6570	12.876	2.8928	1.2134	11.230	0.92423	0.34304	10.618	0.13553	0.048269	10.485
9.0771	7.5516	24.427	5.0804	2.5720	12.757	2.7119	1.1232	11.151	0.86572	0.32030	10.604	0.10561	0.037557	10.478
8.8619	7.2786	23.501	4.9649	2.4836	12.636	2.6027	1.0700	11.106	0.82684	0.30527	10.595			
$T = 370 \text{ K}$														
29.959	11.991	48.814	10.821	6.1302	21.036	5.7904	2.4725	13.615	2.4745	0.89065	11.879	0.74262	0.24842	11.450
27.478	11.666	46.379	10.524	5.8971	20.405	5.5672	2.3467	13.442	2.3487	0.84060	11.840	0.63950	0.21305	11.436
25.448	11.363	44.242	10.125	5.5792	19.570	5.3037	2.2024	13.255	2.2039	0.78370	11.797	0.59882	0.19918	11.430
23.709	11.071	42.285	9.7643	5.2882	18.862	5.0318	2.0581	13.072	2.0398	0.72014	11.752	0.56225	0.18675	11.430
20.693	10.465	38.582	9.4634	5.0457	18.297	4.8291	1.9534	12.946	1.8904	0.66311	11.711	0.51947	0.17225	11.418
18.821	9.9990	35.995	9.1063	4.7601	17.645	4.6428	1.8593	12.835	1.7921	0.62596	11.680	0.48560	0.16081	11.418
17.164	9.5011	33.480	8.8485	4.5565	17.219	4.4082	1.7435	12.698	1.6916	0.58831	11.658	0.43973	0.14536	11.403
15.969	9.0748	31.489	8.5893	4.3550	16.805	4.2568	1.6703	12.623	1.5440	0.53364	11.617	0.40072	0.13226	11.401
15.324	8.8144	30.329	8.2504	4.0972	16.295	4.0106	1.5539	12.497	1.4442	0.49709	11.598	0.37336	0.12310	11.395
14.733	8.5537	29.235	8.0201	3.9263	15.970	3.7497	1.4338	12.377	1.3568	0.46530	11.578	0.34669	0.11419	11.388
14.179	8.2876	28.170	7.6729	3.6755	15.508	3.5718	1.3538	12.292	1.2450	0.42499	11.552	0.32051	0.10546	11.385
13.112	7.7083	26.008	7.3602	3.4574	15.129	3.4131	1.2837	12.228	1.1451	0.38930	11.528	0.27777	0.091250	11.378
12.696	7.4555	25.117	7.0650	3.2581	14.802	3.2538	1.2144	12.160	1.0613	0.35957	11.509	0.25053	0.082214	11.374
12.311	7.2084	24.276	6.8002	3.0851	14.517	3.0976	1.1475	12.102	0.95722	0.32296	11.492	0.21978	0.072038	11.368
11.948	6.9623	23.495	6.5029	2.8970	14.221	2.9500	1.0853	12.044	0.89721	0.30198	11.483	0.18032	0.059018	11.363
11.584	6.7042	22.696	6.2282	2.7291	13.978	2.7354	0.99634	11.968	0.85113	0.28595	11.471	0.14746	0.048202	11.356
11.121	6.3610	21.682	5.9621	2.5716	13.746	2.6602	0.96558	11.942	0.79053	0.26494	11.457	0.11332	0.036995	11.348
$T = 400 \text{ K}$														
29.228	10.694	40.859	12.272	5.4481	20.210	5.4042	1.9354	13.845	2.2400	0.72091	12.626	0.58320	0.17838	12.268
27.359	10.385	39.012	11.864	5.2256	19.686	5.1785	1.8398	13.726	2.0547	0.65742	12.576	0.53915	0.16469	12.262
25.689	10.079	37.349	11.425	4.9839	19.125	4.9731	1.7542	13.626	1.8965	0.60378	12.537	0.49306	0.15040	12.255
24.246	9.7862	35.793	11.009	4.7534	18.607	4.7834	1.6761	13.541	1.7972	0.57039	12.514	0.45222	0.13778	12.249
22.931	9.4915	34.351	10.615	4.5359	18.140	4.5824	1.5945	13.448	1.6735	0.52908	12.485	0.41295	0.12567	12.241
21.765	9.2048	32.988	10.232	4.3247	17.709	4.3526	1.5026	13.350	1.5729	0.49573	12.460	0.37905	0.11524	12.234
20.714	8.9221	31.710	9.8371	4.1089	17.281	4.1684	1.4299	13.271	1.4913	0.46882	12.438	0.34031	0.10334	12.231
19.765	8.6448	30.538	9.4356	3.8917	16.863	3.9880	1.3596	13.199	1.3860	0.43430	12.420	0.31322	0.095041	12.229
18.892	8.3681	29.423	9.0600	3.6912	16.498	3.7784	1.2790	13.118	1.2793	0.39958	12.393	0.29091	0.088214	12.219
18.095	8.0964	28.359	8.6828	3.4930	16.145	3.6698	1.2378	13.081	1.1746	0.36569	12.374	0.25628	0.077635	12.217
17.258	7.7884	27.218	8.2162	3.2525	15.739	3.5168	1.1801	13.030	1.0482	0.32510	12.353	0.22010	0.066603	12.205
16.442	7.4655	26.082	7.7676	3.0268	15.374	3.3409	1.1145	12.963	0.93577	0.28924	12.328	0.17206	0.051994	12.197
15.650	7.1286	24.976	7.3327	2.8135	15.041	3.1945	1.0605	12.914	0.88281	0.27244	12.319	0.14304	0.043187	12.196
15.072	6.8682	24.130	6.8700	2.5926	14.719	3.0035	0.99082	12.849	0.82812	0.25514	12.308	0.11397	0.034381	12.186
14.540	6.6174	23.377	6.4653	2.4047	14.452	2.8418	0.93252	12.801	0.76942	0.23664	12.302			
14.034	6.3700	22.657	6.1670	2.2694	14.269	2.6745	0.87286	12.751	0.69700	0.21390	12.285			
13.189	5.9380	21.469	5.9022	2.1515	14.113	2.5330	0.82291	12.709	0.65091	0.19949	12.281			
12.725	5.6926	20.829	5.6467	2.0397	13.972	2.3921	0.77362	12.668	0.61260	0.18753	12.274			
$T = 430 \text{ K}$														
30.906	9.8640	37.098	13.394	4.9629	19.970	5.7393	1.8375	14.595	2.4281	0.71818	13.466	0.67006	0.19027	13.100
29.313	9.5936	35.728	12.882	4.7467	19.498	5.4777	1.7428	14.476	2.2914	0.67558	13.432	0.60744	0.17225	13.088
27.712	9.2983	34.317	12.362	4.5253	19.017	5.1054	1.6099	14.321	2.0968	0.61538	13.384	0.57247	0.16220	13.084
26.291	9.0133	32.995	11.839	4.3018	18.552	4.7860	1.4976	14.204	1.9247	0.56261	13.350	0.52175	0.14766	13.078
24.931	8.7176	31.734	11.360	4.0972	18.155	4.4921	1.3958	14.094	1.8180	0.53008	13.321	0.46050	0.13014	13.070
23.636	8.4127	30.478	10.894	3.8987	17.771	4.3438	1.3449	14.041	1.7171	0.49948	13.298	0.42922	0.12122	13.061
22.413	8.1014	29.262	10.163	3.5887	17.209	4.1106	1.2656	13.959	1.6208	0.47042	13.279	0.40010	0.11292	13.055
21.171	7.7595	27.994	9.5985	3.3523	16.790	3.9545	1.2129	13.909	1.5308	0.44338	13.261	0.36036	0.10161	13.047
20.081	7.4362	26.868	9.0568	3.1280	16.422	3.8313	1.1717	13.867	1.4464	0.41811	13.243	0.33820	0.095317	13.044
19.231	7.1685	25.984	8.6710	2.9702	16.168	3.6569	1.1137	13.816	1.3484	0.38891	13.222	0.31445	0.088576	13.039
18.351	6.8762	25.052	8.2924	2.8171	15.933	3.5079	1.0645	13.762	1.1809	0.33929	13.186	0.28470	0.080142	13.037
17.527	6.5882	24.186	7.7872	2.6157	15.630	3.3566	1.0149	13.720	1.0874	0.31175	13.170	0.24821	0.069813	13.029
16.743	6.3018	23.359	7.3226	2.4336	15.369	3.1946	0.96222	13.675	0.97656	0.27925	13.150	0.22094	0.062104	13.025
16.025	6.0295	22.601	6.9321	2.2830	15.166	3.0532	0.91653	13.630	0.90570	0.25857	13.137	0.18679	0.052466	13.017
15.400	5.7854	21.957	6.6133	2.1618	15.002	2.8986	0.86694	13.584	0.86264	0.24604	13.132	0.13854	0.038871	13.004
14.772	5.5333	21.307	6.3101	2.0480	14.847	2.7242	0.81140	13.542	0.78392	0.22318	13.117			
14.177	5.2895	20.727	6.0143	1.9383	14.713	2.5735	0.76381	13.502	0.73774	0.20981	13.109			

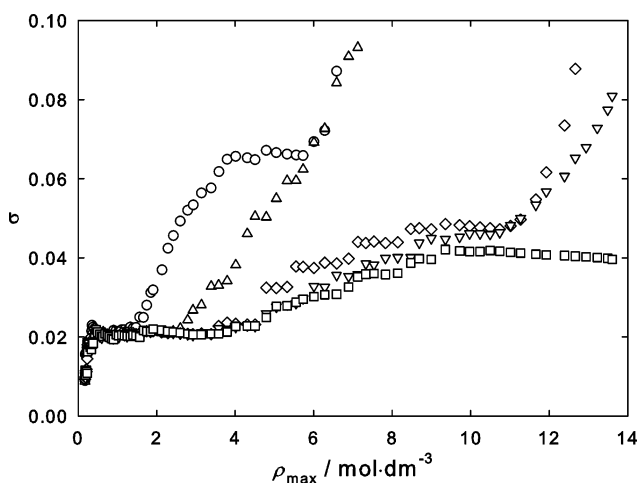
<sup>a</sup> Excluded from polynomial fit.

be established that the results of nearly all viscosity measurements, using temperature and pressure measurements to determine the density, are influenced in the same way. This problem

could be avoided by direct density measurements in addition to that of the viscosity resulting in triples of  $(T, \rho, \eta)$  as noticed in the Conclusion.



**Figure 1.** Evaluation of the 300 K isotherm with a power series expansion in the reduced density  $\delta$  (eq 1). Representation of the weighted standard deviation ( $\sigma$ ) as a function of the maximum molar density ( $\rho_{\max}$ ) for which experimental points are included:  $\circ$ , first order in  $\delta$ ;  $\triangle$ , second order in  $\delta$ ;  $\diamond$ , third order in  $\delta$ ;  $\nabla$ , fourth order in  $\delta$ .



**Figure 2.** Evaluation of the 320 K isotherm with a power series expansion in the reduced density  $\delta$  (eq 1). Representation of the weighted standard deviation ( $\sigma$ ) as a function of the maximum molar density ( $\rho_{\max}$ ) for which experimental points are included:  $\circ$ , second order in  $\delta$ ;  $\triangle$ , third order in  $\delta$ ;  $\diamond$ , fourth order in  $\delta$ ;  $\nabla$ , fifth order in  $\delta$ ;  $\square$ , sixth order in  $\delta$ .

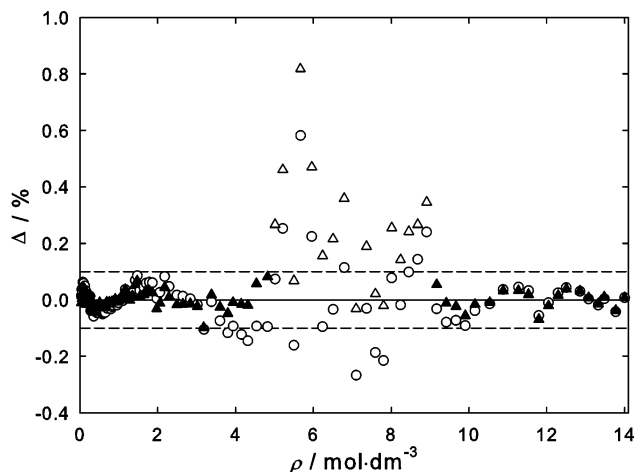
In Table 2, the order in  $\delta$  of the series expansion, needed for an appropriate description of all eight isotherms, and the values of the coefficients  $\eta_i$  are listed. It is evident that the first density coefficient  $\eta_1$  shows a distinct temperature dependence, whereas the temperature has only a weak impact on the higher coefficients.

With respect to a comparison with data from the literature discussed below, the experimental data of all isotherms apart from that excluded for the 310 K isotherm were correlated with a double polynomial series expansion according to the following equation for which the coefficients  $\eta_{ij}$  are given in Table 3:

$$\eta(\tau, \delta) = \sum_{i=0}^6 \sum_{j=0}^2 \eta_{ij} \frac{\delta^i}{\tau^j} \quad (2)$$

### Comparison with Literature

The new experimental data of ethane have been compared with the most accurate correlations and experimental data available in the literature. Figure 4 shows a comparison of reliable low-density viscosity data from the literature and of



**Figure 3.** Evaluation of the 310 K isotherm with a power series expansion of the sixth order in the reduced density  $\delta$  (eq 1). Deviations [ $\Delta = 100(\eta_{\text{exp}} - \eta_{\text{fit}})/\eta_{\text{fit}}$ ] as a function of the molar density ( $\rho$ ):  $\circ$ , all data included in fit;  $\blacktriangle$ , critical region excluded from fit;  $\triangle$ , recalculated points of critical region.

the correlated values by Friend et al.<sup>2</sup> as well as of the present data, all near to atmospheric pressure, with the correlation by Hendl et al.<sup>3</sup> The figure makes evident that most of the data agree with the correlation by Hendl et al. within  $\pm 0.3\%$ . The data by Eakin et al.<sup>16</sup> and by Carmichael and Sage<sup>17</sup> show larger deviations ( $< -0.5\%$  and  $> +0.5\%$ ) due to the fact that these measurements were mostly performed at higher pressures. Analogously the data by Hunter and Smith<sup>21</sup> are characterized by larger deviations ( $< -0.5\%$ ), because these measurements were carried out down to low temperatures. Furthermore, the data by Kestin et al.<sup>19</sup> and Abe et al.<sup>20</sup> deviate above 320 K from the correlation by Hendl et al.<sup>3</sup> by more than  $+0.5\%$  due to an error in their temperature measurement with thermocouples (see Vogel et al.<sup>23</sup>). In addition, the correlated values by Friend et al.<sup>2</sup> show remarkably large differences to the correlation by Hendl et al. near room temperature as well as large deviations from the data by Kestin and co-workers,<sup>18–20</sup> which this correlation is based on. The reason for this behavior is that Friend et al.<sup>2</sup> used for the representation of the zero-density viscosity contribution a 11–6–8 potential function ( $\gamma = 3.0$ ) with only two adjustable parameters ( $\epsilon$  and  $\sigma$ ). Such a fitting function is too inflexible to describe the experimental zero-density viscosity values in an adequate manner. On the other hand, the representation of the experimental data by Hendl et al.<sup>3</sup> based on the theorem of corresponding states using a combination of a universal and an individual correlation, is more suitable.<sup>23</sup> Finally, the results, obtained by Hendl and Vogel<sup>22</sup> by means of an oscillating-disk viscometer in our laboratory more than 10 years ago and the present values agree within  $\pm 0.2\%$ .

Figure 5 and Figure 6 illustrate the deviations of the present experimental values from the correlation of Friend et al.<sup>2</sup> (upper diagram) as well as from the correlation of Hendl et al.<sup>3</sup> (lower diagram) as a function of pressure ( $p$ ) and as a function of molar density ( $\rho$ ), respectively. With regard to the correlation of Friend et al.,<sup>2</sup> the maximum differences of the subcritical isotherms in Figure 5 (upper diagram) amount to  $-5.3\%$ , whereas the supercritical isotherm at 310 K shows a maximum difference of approximately  $-5.2\%$  near to the critical pressure ( $p_c = 4.8722 \text{ MPa}$ )<sup>1</sup> corresponding to a density around  $4 \text{ mol}\cdot\text{dm}^{-3}$  in Figure 6 (upper diagram). The higher isotherms above 350 K are characterized by differences between  $-(1 \text{ and } 3)\%$  at higher pressures and densities. The deviation curves in the lower

Table 2. Coefficients of Equation 1

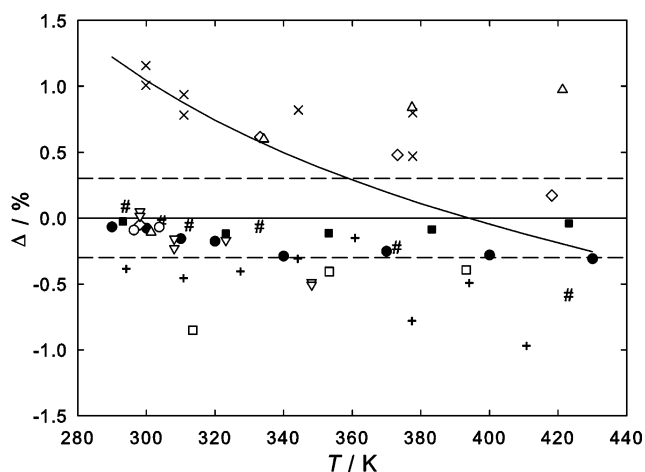
$T$ K	$n$	$\rho_{\max}$ $\text{mol}\cdot\text{dm}^{-3}$	$\eta_0$ $\mu\text{Pa}\cdot\text{s}$	$\eta_1$ $\mu\text{Pa}\cdot\text{s}$	$\eta_2$ $\mu\text{Pa}\cdot\text{s}$	$\eta_3$ $\mu\text{Pa}\cdot\text{s}$	$\eta_4$ $\mu\text{Pa}\cdot\text{s}$	$\eta_5$ $\mu\text{Pa}\cdot\text{s}$	$\eta_6$ $\mu\text{Pa}\cdot\text{s}$	$\sigma^a$
290	3	1.76	$8.992 \pm 0.001$	$1.230 \pm 0.023$	$13.025 \pm 0.226$	$-8.231 \pm 0.601$				0.016
300	3	2.56	$9.295 \pm 0.001$	$1.581 \pm 0.018$	$11.610 \pm 0.128$	$-3.900 \pm 0.241$				0.020
310	6	14.00	$9.590 \pm 0.001$	$1.829 \pm 0.025$	$11.806 \pm 0.164$	$-7.029 \pm 0.405$	$7.775 \pm 0.436$	$-3.800 \pm 0.212$	$0.879 \pm 0.038$	0.031
320	6	13.60	$9.887 \pm 0.001$	$1.982 \pm 0.033$	$12.033 \pm 0.204$	$-7.669 \pm 0.495$	$8.098 \pm 0.547$	$-3.798 \pm 0.276$	$0.858 \pm 0.052$	0.040
340	6	12.64	$10.470 \pm 0.001$	$2.399 \pm 0.027$	$11.628 \pm 0.176$	$-6.966 \pm 0.454$	$7.047 \pm 0.535$	$-3.193 \pm 0.289$	$0.742 \pm 0.058$	0.029
370	5	11.99	$11.334 \pm 0.001$	$2.959 \pm 0.028$	$10.114 \pm 0.141$	$-2.817 \pm 0.261$	$1.307 \pm 0.196$	$0.255 \pm 0.051$		0.040
400	4	10.69	$12.175 \pm 0.001$	$3.259 \pm 0.013$	$10.288 \pm 0.049$	$-3.834 \pm 0.060$	$2.213 \pm 0.022$			0.027
430	4	9.86	$12.993 \pm 0.001$	$3.497 \pm 0.013$	$10.069 \pm 0.051$	$-3.792 \pm 0.066$	$2.223 \pm 0.026$			0.023

<sup>a</sup> Weighted.

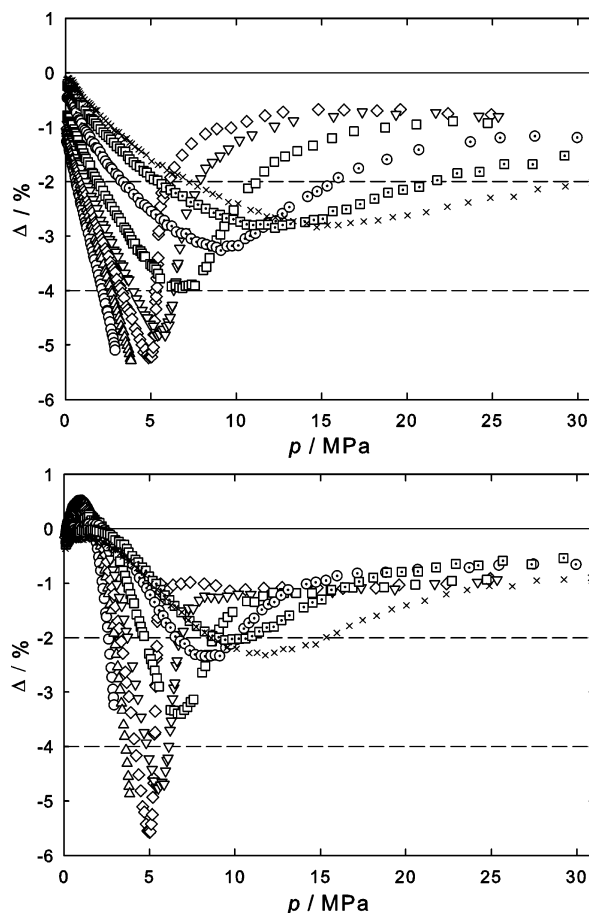
Table 3. Coefficients of Equation 2

$i$	$\eta_{i0}$ $\mu\text{Pa}\cdot\text{s}$	$\eta_{i1}$ $\mu\text{Pa}\cdot\text{s}$	$\eta_{i2}$ $\mu\text{Pa}\cdot\text{s}$
0	29.596	-31.366	11.214
1	3.379	4.359	-6.064
2	10.702	-3.057	4.505
3	3.528	-18.919	7.937
4	-16.650	45.523	-20.952
5	15.163	-36.482	17.598
6	-3.729	9.145	-4.577

diagrams of Figures 5 and 6, which are related to the correlation of Hendl et al.,<sup>3</sup> look quite similar due to nearly the same database used to derive the surface correlations. But there is a large difference in the low-density range in which the deviation curves related to the correlation of Hendl et al.<sup>3</sup> show a distinct bump. This is caused by a different way to take into account the initial density dependence of the viscosity. Hendl et al. used the Rainwater–Friend theory,<sup>24–26</sup> which is designed to represent the correct temperature dependence of the initial density viscosity coefficient  $\eta_1$  at low reduced temperatures  $T^* = (k_B T)/\epsilon$  in an appropriate manner. (Here  $\epsilon$  is an energy scaling factor, and  $k_B$  is Boltzmann's constant.) In the contrary, Friend et al. used a more unspecific representation for the initial density dependence with practically no temperature dependence. A closer look at the subcritical isotherms in Figure 5 (lower diagram) shows deviations up to only -3.2 % for the 290 K and up to -4.9 % at moderate densities. The supercritical isotherm at 310 K deviates up to -5.6 % from the correlation of Hendl et al., again near to the critical pressure (Figure 5)



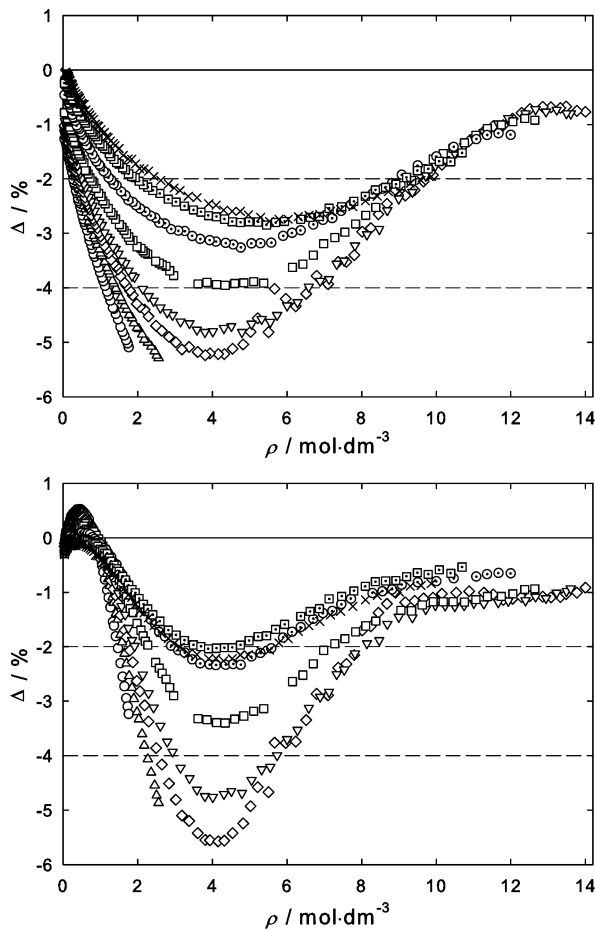
**Figure 4.** Comparison of reliable experimental low-density viscosity data and of the correlated values by Friend et al.<sup>2</sup> with the correlation by Hendl et al.<sup>3</sup> Deviations [ $\Delta = 100(\eta_{\text{exp}} - \eta_{\text{cor}})/\eta_{\text{cor}}$ ] as a function of temperature ( $T$ ). Experimental data: #, Meshcheryakov and Golubev;<sup>15</sup> +, Eakin et al.;<sup>16</sup> x, Carmichael and Sage;<sup>17</sup> O, Kestin et al.;<sup>18</sup> Δ, Kestin et al.;<sup>19</sup> ◇, Abe et al.;<sup>20</sup> ▽, Iwasaki and Takahashi;<sup>14</sup> □, Hunter and Smith;<sup>21</sup> ■, Hendl and Vogel;<sup>22</sup> ●, this work; —, correlation by Friend et al.<sup>2</sup>



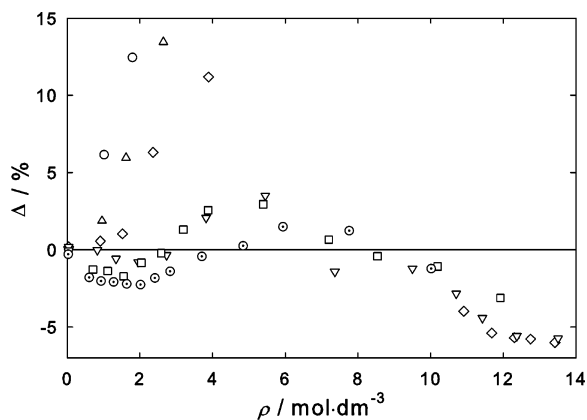
**Figure 5.** Comparison of experimental viscosity data of the present work at different temperatures with the viscosity surface correlations by Friend et al.<sup>2</sup> (upper diagram) and Hendl et al.<sup>3</sup> (lower diagram). Deviations [ $\Delta = 100(\eta_{\text{exp}} - \eta_{\text{cor}})/\eta_{\text{cor}}$ ] as a function of pressure ( $p$ ): O, 290 K; Δ, 300 K; ◇, 310 K; ▽, 320 K; □, 340 K; ⊙, 370 K; ⊠, 400 K; x, 430 K.

and to the molar density of  $4 \text{ mol}\cdot\text{dm}^{-3}$  (Figure 6). The differences for the higher isotherms above 350 K amount to values of only  $-(0.5 \text{ to } 2.3) \%$  at higher pressures and densities. In summary, the maximum differences of our values from both correlations occur in regions with large values of the isothermal compressibility. This does not mean that only the data of this paper are influenced by small errors in temperature and pressure, but that the other values considered in the data correlation are also affected by such uncertainties. Consequently, there is a strong need for new and very accurate measurements in this thermodynamic range.

Furthermore, the experimental values of this paper fitted with eq 2 have been compared with data mostly used for the development of the surface correlations. It is demonstrated in Figures 7 to 11 that there exist only a few measurements, the techniques of which (given in brackets) are characterized by



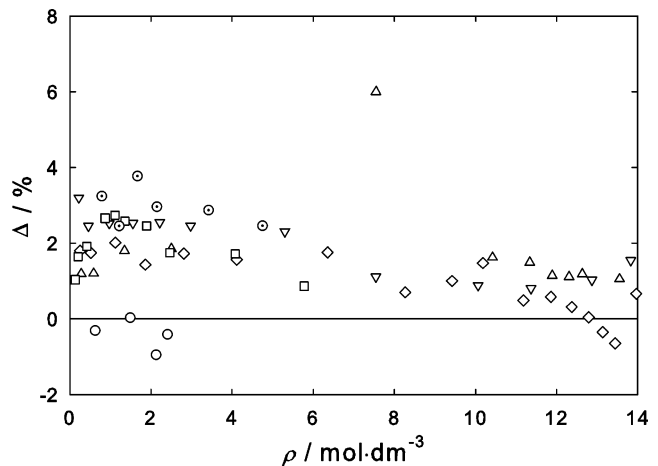
**Figure 6.** Comparison of experimental viscosity data of the present work at different temperatures with the viscosity surface correlations by Friend et al.<sup>2</sup> (upper diagram) and Hendl et al.<sup>3</sup> (lower diagram). Deviations [ $\Delta = 100(\eta_{\text{exp}} - \eta_{\text{cor}})/\eta_{\text{cor}}$ ] as a function of molar density ( $\rho$ ): ○, 290 K; △, 300 K; ◇, 310 K; ▽, 320 K; □, 340 K; ⊙, 370 K; ⊞, 400 K; ×, 430 K.



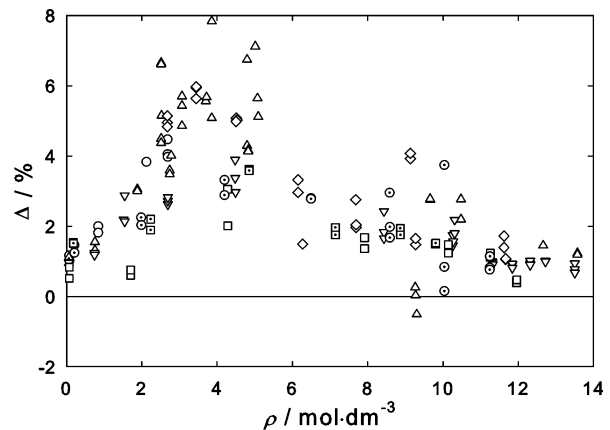
**Figure 7.** Comparison of the experimental viscosity data by Meshcheryakov and Golubev<sup>15</sup> with the results of the present paper. Deviations [ $\Delta = 100(\eta_{\text{lit}} - \eta_{\text{present}})/\eta_{\text{present}}$ ] as a function of molar density ( $\rho$ ): ○, 294 K; △, 305 K; ◇, 313 K; ▽, 333 K; □, 373 K; ⊙, 423 K.

an adequate accuracy. These are the data by Meshcheryakov and Golubev<sup>15</sup> (capillary), by Eakin et al.<sup>16</sup> (capillary), by Carmichael and Sage<sup>17</sup> (rotating cylinder), by Iwasaki and Takahashi<sup>14</sup> (oscillating disk), and by Diller and Ely<sup>27</sup> (torsional crystal). The deviations of the literature data from the fitted values are shown as a function of molar density ( $\rho$ ).

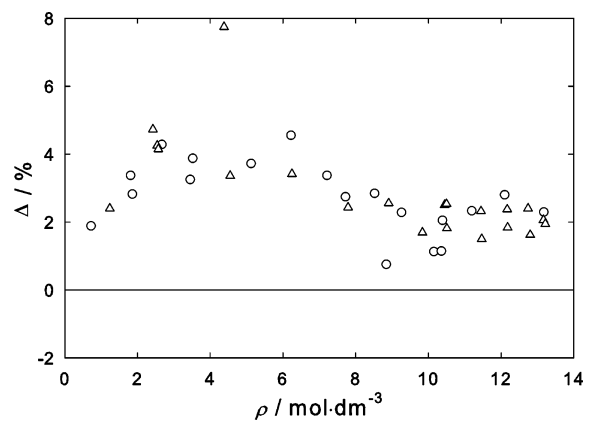
The comparison with the data by Meshcheryakov and Golubev<sup>15</sup> in Figure 7 reveals large deviations of (−6 to +13) % in maximum. Therefore, these data were not included into



**Figure 8.** Comparison of the experimental viscosity data by Eakin et al.<sup>16</sup> with the results of the present paper. Deviations [ $\Delta = 100(\eta_{\text{lit}} - \eta_{\text{present}})/\eta_{\text{present}}$ ] as a function of molar density ( $\rho$ ): ○, 298 K; △, 311 K; ◇, 344 K; ▽, 378 K; □, 411 K; ⊙, 444 K.

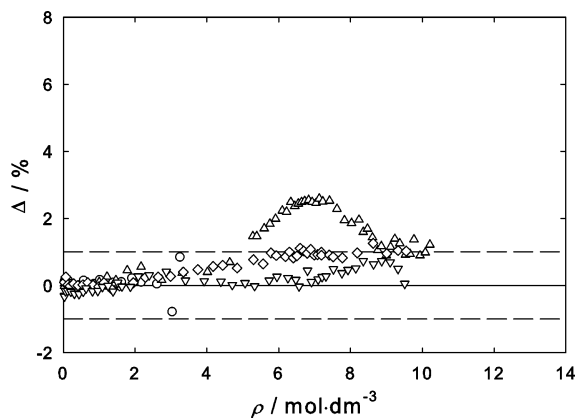


**Figure 9.** Comparison of the experimental viscosity data by Carmichael and Sage<sup>17</sup> with the results of the present paper. Deviations [ $\Delta = 100(\eta_{\text{lit}} - \eta_{\text{present}})/\eta_{\text{present}}$ ] as a function of molar density ( $\rho$ ): ○, 300 K; △, 311 K; ◇, 328 K; ▽, 344 K; □, 378 K; ⊙, 411 K; ⊞, 444 K.



**Figure 10.** Comparison of the experimental viscosity data by Diller and Ely<sup>27</sup> with the results of the present paper. Deviations [ $\Delta = 100(\eta_{\text{lit}} - \eta_{\text{present}})/\eta_{\text{present}}$ ] as a function of molar density ( $\rho$ ): ○, 319 K; △, 400 K.

the primary data sets of the correlations discussed before, although the deviations are somewhat smaller at intermediate densities. Figure 8 concerning the comparison with the experimental data by Eakin et al.<sup>16</sup> shows differences in the range from (−1 to +4) %. In addition, there is an outlier of +6 % at 311 K near to the critical density. Figure 9 illustrates a systematic trend in the deviations of the data by Carmichael



**Figure 11.** Comparison of the experimental viscosity data by Iwasaki and Takahashi<sup>14</sup> with the results of the present paper. Deviations [ $\Delta = 100(\eta_{\text{lit}} - \eta_{\text{present}})/\eta_{\text{present}}$ ] as a function of molar density ( $\rho$ ):  $\circ$ , 298 K;  $\triangle$ , 308 K;  $\diamond$ , 323 K;  $\nabla$ , 348 K.

and Sage<sup>17</sup> from the results of the present paper with a maximum of 8 % at a density around 4 mol·dm<sup>-3</sup>. In addition, the deviations are characterized by a rather large scattering of up to 5 %. The two supercritical isotherms by Diller and Ely<sup>27</sup> at (319 and 400) K, which are compared with the data of the present paper in Figure 10, deviate systematically to positive values of (1 to 5) %, with an outlier of 8 % at a density of 4 mol·dm<sup>-3</sup>. As a summary, it is to be stated that the data included in the surface correlations of the literature differ from the values of the present paper in a systematic way with deviations of +(1 to 2) % in the average, apart from densities somewhat smaller than the critical one. This is certainly due to the influence of the high isothermal compressibility near to the critical region.

The best agreement with data from the literature has been found with those by Iwasaki and Takahashi<sup>14</sup> as shown in Figure 11. Surprisingly, these values were not included in the primary data sets used for the surface correlations by Friend et al.<sup>2</sup> and Hendl et al.<sup>3</sup> These measurements were focused on the investigation of the critical enhancement of the viscosity of ethane. Even if measuring problems occurred very close to the critical point, there is certainly no reason to doubt about the reliability of these measurements a priori. We have restricted the comparison to temperatures not too close to the critical one. For the temperatures considered our values agree within (-0.3 to +1) % for densities up to 10 mol·dm<sup>-3</sup> with the data by Iwasaki and Takahashi,<sup>14</sup> except for the 308 K isotherm for which the deviations arise up to only +2.5 % near the critical density. We believe that the measurements by Iwasaki and Takahashi<sup>14</sup> and our own are not influenced seriously by uncertainties due to the isothermal compressibility at temperatures several degrees distant from the critical one. The agreement between both data sets demonstrated in Figure 11 makes clear that these data should be considered as very accurate and suitable to build the basis of primary data sets for an improved viscosity surface correlation. The discussion concerning the deviations between the different data sets makes evident that there is a real need for new measurements of high precision to improve the viscosity surface correlation for ethane.

## Conclusions

In general, the reproducibility and the uncertainty of the viscosity measurements with the vibrating-wire viscometer in the vapor phase and at supercritical temperatures amount to  $\pm$  (0.05 to 0.1) % and  $\pm$  (0.25 to 0.4) %. However, at temperatures (5 to 10) K above the critical one and near to the critical density, a distinct increase of the uncertainty possibly up to (1 to 2) %

has to be accepted. The high isothermal compressibility in this thermodynamic region connected with small uncertainties of the measured pressures and temperatures is responsible for comparably high uncertainties in the calculated densities needed for the evaluation of the viscosity. Therefore, the experimental equipment for the viscosity measurements will be completed by a simultaneous density measurement, using the single-sinker method based on the buoyancy principle,<sup>28</sup> to provide triples in ( $T$ ,  $\rho$ ,  $\eta$ ).

The data included in the development of the viscosity surface correlations by Friend et al.<sup>2</sup> and by Hendl et al.<sup>3</sup> are represented by these correlations within  $\pm 2.5$  % apart from the region close to the critical point. However, not only the older data by Iwasaki and Takahashi<sup>14</sup> but also the new values of the present paper deviate by about -2.5 % on the average from the recommended surface correlations as well as from the primary data sets included in the development of those surface correlations. This systematic difference and the high accuracy of the measuring techniques used by Iwasaki and Takahashi<sup>14</sup> and in the present paper justify a reevaluation of the surface correlation for ethane with a suitable database extended by further measurements.

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Received for review July 20, 2005. Accepted September 26, 2005.

JE050287L