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Viscosity Measurements and Predictions for Natural Gas[1]

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A vibrating-wire viscometer of very high precision was used to measure the viscosity of methane and of two natural gases. The experimental data were, in general, taken at temperatures of 260, 280, 300, and 320 K and at pressures up to 20 MPa, and additionally in the case of methane at temperatures of 340 and 360 K and at pressures up to 29 MPa. The estimated uncertainty is ±0.3 and ±0.5% for methane and the natural gases, respectively. The new experimental data for methane were used together with zero-density or low-density viscosity values from this study and from the literature to develop a viscosity equation for natural gas composed of two contributions. The mixing rule of Wilke [J. Chem. Phys. 18: 517 1950] was applied for the zero-density viscosity part which is based on zero-density correlations for twelve components (methane, nitrogen, carbon dioxide, ethane, propane, n- and isobutane, n- and isopentane, n-hexane, n-heptane, and n-octane) and agrees with the values derived from experiment within ±0.3%. The density dependence of the residual viscosity part was correlated with methane data only, neglecting any temperature dependence, whereas the composition dependence is characterized by a pseudo-critical viscosity value. For methane the agreement between the correlated and experimental data is within ±0.5%. The values predicted with the correlation and the experimental data agree within ±1% for both the high calorific, H, natural gas and the low calorific, L, natural gas.

KEY WORDS: correlation; measurement; methane; natural gases; vibrating-wire viscometer; viscosity.

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1. INTRODUCTION

Thermodynamic properties of methane as the main component of natural gas and of natural gas itself have frequently been investigated because of its industrial importance. The most recent equations of state for thermodynamic properties were reported for methane by Friend et al. [1] and by Wagner and de Reuck [2] and for natural gas by Jaeschke et al. [3,4] and by Starling and Savidge [5]. These equations are now routinely applied in energy billing. Particularly with the help of these equations, the volume metered under varying actual field conditions is converted to well defined reference conditions.

In addition to the thermodynamic properties, Friend et al. [1] correlated the experimental transport property values, for the viscosity as well as for the thermal conductivity, of methane. However, the transport property data are not of the same high accuracy as the thermodynamic data. Consequently, there has been a steady demand for new high-accuracy values and for their correlation connected with a critical assessment of the available data.

A vibrating-wire viscometer designed by Wilhelm et al. [6] 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 [7,8]. The measuring program was then extended to methane [9] and two natural gases [10] in a thermodynamic range which is of particular interest for the gas industry. A suitable experimental procedure had to be developed in order to minimize the influence of the retrograde behavior and the effects of adsorption and desorption that have to be expected in that thermodynamic range for natural gases. This experience and a suitable measuring procedure starting from vacuum followed by successive points up to the maximum pressure has been discussed [10]. In the present paper the experimental data for methane as well as for both natural gas specimens are reported. The new experimental data for methane are used together with literature data to develop a correlation for a limited pressure and temperature range (up to 30 MPa and from 250 to 450 K) which allows prediction of the experimental viscosity data of natural gases nearly within the experimental uncertainty.

2. VIBRATING-WIRE VISCOMETER

Since the details of the instrument have been given by Wilhelm et al. [6] and Wilhelm and Vogel [7], it is sufficient to summarize only the essential features here. The wire is placed in a magnetic field in such a manner that even harmonics cannot be initiated due to the symmetric arrangement of the wire and field and that the third harmonic mode of the oscillation is suppressed using a ratio of 1.5 between the lengths of the wire and field. The wire material has been chosen to be Chromel instead of tungsten conventionally used for measurements in liquids. The reason is that the rough surface of tungsten causes systematic errors in measurements on dilute gases and even dense gases. The oscillation is initiated by a sinusoidal voltage pulse at a frequency close to the resonant 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, a hundred runs are recorded and the measured oscillation curves are averaged. Here it is assumed that the noise is asynchronous. An important point is that comparably large displacements y of the wire compared with its radius R are necessary in order to obtain reasonably large measuring signals. This is in contradiction to the requirements of the measuring theory that the displacement should be only on the order of 1% of the radius of the wire. Wilhelm et al. have shown that the parameters of the oscillation curves, the logarithmic decrement Δ and the frequency ω, depend on the square of the relative initial amplitude $\varepsilon = y_{\max}/R$. Therefore, they used relatively large and different values of ε in the oscillation runs and determined the correct values of Δ and ω by extrapolation of the values for the different runs as a function of $\varepsilon^2 \to 0$.

The viscometer cell is suspended from the top closure of a pressure vessel which is placed in a heat-pipe thermostat filled either with methanol or water depending on the temperature range of the measurements. The temperature is determined with an uncertainty of ±0.015 K by means of a premium ITS-90 thermometer and a 6½ digit multimeter. The pressure vessel is connected with four pressure transmitters supplied by Digiquartz, which are characterized by an uncertainty of 0.01% of reading and of 0.01% of full scale.

The theory of the vibrating-wire viscometer developed by Retsina et al. [11] relates the properties of the fluid, the density ρ and the viscosity η, to the parameters of the damped harmonic oscillation Δ and ω. The resulting working equations may be used to calculate the viscosity from the measured values Δ and ω provided 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 are known. An accurate wire radius R cannot be obtained by direct measurements. Hence, it has been determined as 12.765 μm by means of viscosity measurements on argon at room temperature using reference values by Kestin and Leidenfrost [12] assuming the density of the wire material Chromel to be 8500 $\mathrm{kg \cdot m^{-3}}$ as given by the supplier. The reproducibility of the measurements is better than ±0.1%, whereas the uncertainty is assumed to be ±0.2%. This is valid for gases for which the density can be reliably deduced from the temperature and pressure values of the measurements.

3. MEASUREMENTS AND RESULTS

The viscosity coefficient of methane and of two natural gases, a low calorific, L, natural gas and a high calorific, H, natural gas, were measured with the high precision vibrating-wire viscometer at the University of Rostock. The certified purity of methane supplied by Messer Griesheim (Germany) was 99.994%. The densities ρ were calculated from the measured pressures p and temperatures T with the equation of state by Wagner and de Reuck [2]. The uncertainty in calculated density is ± 0.03–0.07%.

The molar-composition analysis of the two natural gases was performed with a gas chromatograph by Ruhrgas AG. The molar compositions of the samples H and L including the relative uncertainties of the components are listed in Table I. The densities of the natural gas samples were calculated with an uncertainty of ±0.1% from the measured temperatures and pressures using the International Standard ISO 12213 [13,5], assuming that the input variables temperature, pressure, and molar composition are known with negligible uncertainty. An additional uncertainty of ±0.1% is to be expected in the case that the uncertainties of the measured temperatures and pressures are approximately ±0.15 K and ±0.02 MPa and that the uncertainties in mole fractions are reasonably small. Hence, the uncertainty of the calculated densities is estimated to be generally ±0.2 and ±0.3% at the higher pressures for low temperatures as discussed in more detail by Vogel et al. [10].

Four isothermal series of measurements for methane as well as for each natural gas were performed at nominal temperatures of 260, 280, 300, and 320 K and at pressures up to 20 MPa. In addition, two isothermal series of measurements for methane were carried out at nominal temperatures of 340 and 360 K and at pressures up to 29 MPa. Each series comprises about 60 data points. The individual points were not measured exactly at the nominal temperatures, but were corrected to isothermal values by means of a Taylor expansion restricted to the first power in temperature. 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 methane are listed in Table II, whereas the experimental data for natural gases H and L are summarized in Tables III and IV, respectively. The values at pressures below 0.25 MPa are characterized by a tendency to be too low which may be caused by the slip effect. Here, the fluid does not behave as a continuum, since the molecular mean free path is comparable to the wire diameter. The

Table I. Results of the Gas Analysis (in mol%) including its Relative Uncertainties (in %)

Component	mol%	Component	mol%	Component	mol%
H natural gas (Molar mass $M = 17.993$ kg·kmol^{-1})					
Helium	0.0137	Propane	1.2532	Heptanes	0.0340
Carbon dioxide	0.7740	n-Butane	0.1924	Octanes	0.0038
Nitrogen	1.5324	Isobutane	0.2857	Nonanes	0.0010
Oxygen, argon	0.0419	n-Pentane	0.0324	C_{10} plus higher	0.0009
Hydrogen	0.0007	Isopentane	0.0565	Benzene	0.0021
Methane	89.5669	Neopentane	0.0032	Toluene	0.0009
Ethane	6.1464	Hexanes	0.0572	Xylenes	0.0006
L natural gas (Molar mass $M = 18.468$ kg·kmol^{-1})					
Helium	0.0520	Propane	0.6023	Heptanes	0.0174
Carbon dioxide	1.4523	n-Butane	0.1282	Octanes	0.0041
Nitrogen	9.7520	Isobutane	0.1033	Nonanes	0.0021
Oxygen, argon	0.0100	n-Pentane	0.0350	C_{10} plus higher	0.0013
Hydrogen	0.0005	Isopentane	0.0357	Benzene	0.0250
Methane	84.3322	Neopentane	0.0056	Toluene	0.0031
Ethane	3.4085	Hexanes	0.0388	Xylenes	0.0010
Relative uncertainties					
Helium	2.0	Propane	2.5		
Carbon dioxide	1.5	n-Butane	3.0		
Nitrogen	1.5	Isobutane	3.0		
Oxygen, argon	2.0	C_5 plus higher	5.0		
Hydrogen	2.0				
Methane	0.2				
Ethane	2.0				

data influenced by slip are included in the tables, but marked. They were excluded from further evaluation.

With respect to the large number of experimental points, only the pressures, densities and viscosities are given in the tables. We are aware of the fact that the densities should possibly be re-evaluated with an improved equation of state that might be available in the future. The uncertainty of the density propagates into the uncertainty of the viscosity in two ways. First, the density is needed to calculate the viscosity according to the theory of the vibrating-wire viscometer by Retsina et al. [11] using the parameters of the damped harmonic oscillation, Δ and ω. Second, the viscosity is reasonably represented as a function of density. For such a re-evaluation the exact experimental temperatures and pressures as well as Δ and ω, both extrapolated to $\varepsilon^2 \to 0$, are needed. An uncertainty of 0.2% in the density data contributes a change of only 0.1% in the viscosity.

Table II. Experimental Viscosity Values of Methane 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)
$T = 260$ K								
0.10183[a]	0.047240	9.815	3.4829	1.7864	10.499	11.477	7.4763	15.004
0.20109	0.093544	9.836	3.7399	1.9338	10.568	12.013	7.9014	15.482
0.30122	0.14052	9.851	3.9893	2.0792	10.642	12.478	8.2654	15.903
0.39823	0.18628	9.865	4.2620	2.2408	10.733	13.017	8.6799	16.396
0.49718	0.23322	9.879	4.4841	2.3745	10.807	13.501	9.0439	16.846
0.60056	0.28254	9.896	4.7459	2.5345	10.896	13.992	9.4030	17.326
0.70042	0.33046	9.906	4.9951	2.6893	10.988	14.498	9.7620	17.800
0.80001	0.37852	9.924	5.4983	3.0094	11.182	15.008	10.112	18.292
0.89935	0.42674	9.939	5.9963	3.3361	11.394	15.529	10.455	18.786
1.0025	0.47709	9.954	6.5025	3.6785	11.623	16.008	10.759	19.240
1.2521	0.60020	10.000	6.9980	4.0236	11.871	16.541	11.083	19.735
1.5008	0.72469	10.042	7.4996	4.3828	12.141	17.024	11.365	20.192
1.7532	0.85291	10.088	7.9944	4.7463	12.428	17.393	11.572	20.532
1.9979	0.97907	10.135	8.4808	5.1120	12.726	17.989	11.894	21.062
2.2625	1.1176	10.196	9.0077	5.5164	13.072	18.473	12.143	21.496
2.5035	1.2457	10.249	9.4550	5.8655	13.389	18.991	12.399	21.943
2.7332	1.3696	10.302	9.9945	6.2919	13.791	19.471	12.626	22.359
2.9864	1.5082	10.362	10.498	6.6933	14.185	19.825	12.788	22.652
3.2482	1.6538	10.429	11.011	7.1041	14.597			

$T = 280$ K								
0.10051[a]	0.043269	10.484	3.4971	1.6236	11.107	11.496	6.2726	14.482
0.19855	0.085652	10.504	3.7363	1.7441	11.162	11.999	6.5905	14.795
0.30070	0.13001	10.519	3.9981	1.8774	11.235	12.482	6.8953	15.098
0.40049	0.17353	10.536	4.2323	1.9980	11.295	13.001	7.2207	15.440
0.49989	0.21707	10.547	4.4882	2.1311	11.368	13.498	7.5292	15.766
0.60097	0.26154	10.564	4.7439	2.2656	11.440	13.934	7.7979	16.059
0.70066	0.30559	10.574	4.9857	2.3942	11.514	14.475	8.1264	16.431
0.79967	0.34953	10.589	5.4971	2.6704	11.676	15.004	8.4418	16.807
0.90042	0.39444	10.604	5.9993	2.9473	11.845	15.504	8.7348	17.167
0.99794	0.43810	10.619	6.5055	3.2320	12.027	16.004	9.0221	17.523
1.2405	0.54750	10.656	7.0084	3.5203	12.218	16.509	9.3051	17.877
1.4975	0.66472	10.699	7.5047	3.8099	12.421	17.004	9.5763	18.247
1.7457	0.77917	10.742	7.9828	4.0934	12.627	17.502	9.8424	18.596
1.9906	0.89336	10.789	8.5210	4.4174	12.875	17.992	10.097	18.961
2.2261	1.0043	10.832	8.9983	4.7087	13.105	18.511	10.359	19.331
2.4962	1.1330	10.887	9.5004	5.0186	13.361	19.012	10.605	19.686
2.7424	1.2517	10.939	10.004	5.3327	13.625	19.467	10.822	20.006
2.9985	1.3765	10.990	10.503	5.6457	13.902	19.837	10.994	20.268
3.2469	1.4989	11.048	11.006	5.9629	14.190			

Table II. (Continued)

p (MPa)	ρ ($\mathrm{mol \cdot L^{-1}}$)	η ($\mu\mathrm{Pa \cdot s}$)	p (MPa)	ρ ($\mathrm{mol \cdot L^{-1}}$)	η ($\mu\mathrm{Pa \cdot s}$)	p (MPa)	ρ ($\mathrm{mol \cdot L^{-1}}$)	η ($\mu\mathrm{Pa \cdot s}$)
$T = 300$ K								
0.09956[a]	0.039981	11.142	3.4972	1.4874	11.711	11.510	5.4815	14.426
0.20094	0.080834	11.161	3.7517	1.6024	11.767	11.998	5.7392	14.658
0.29999	0.12088	11.173	3.9899	1.7109	11.820	12.500	6.0046	14.898
0.40199	0.16226	11.190	4.2491	1.8299	11.879	12.978	6.2564	15.135
0.50040	0.20232	11.204	4.4954	1.9438	11.939	13.457	6.5076	15.380
0.60010	0.24304	11.216	4.7532	2.0640	12.001	14.022	6.8024	15.672
0.69659	0.28258	11.228	4.9943	2.1772	12.064	14.516	7.0580	15.939
0.79568	0.32332	11.238	5.4946	2.4147	12.197	14.975	7.2936	16.178
0.89768	0.36540	11.253	5.9729	2.6449	12.332	15.479	7.5492	16.457
0.99557	0.40592	11.268	6.4710	2.8878	12.482	15.959	7.7904	16.718
1.2519	0.51266	11.306	7.0009	3.1496	12.648	16.471	8.0441	17.003
1.4914	0.61321	11.342	7.4957	3.3971	12.813	16.978	8.2916	17.296
1.7515	0.72332	11.383	7.9804	3.6421	12.979	17.476	8.5309	17.580
2.0037	0.83103	11.424	8.4641	3.8890	13.155	17.965	8.7622	17.860
2.2508	0.93743	11.468	8.9997	4.1649	13.357	18.473	8.9978	18.151
2.4943	1.0431	11.511	9.4997	4.4245	13.554	18.941	9.2110	18.420
2.7374	1.1495	11.558	9.9862	4.6787	13.755	19.525	9.4715	18.755
2.9925	1.2620	11.605	10.487	4.9418	13.968	20.028	9.6910	19.048
3.2483	1.3758	11.657	10.947	5.1843	14.172			

$T = 320$ K								
0.09717[a]	0.036567	11.773	3.4926	1.3733	12.303	11.496	4.8988	14.586
0.20138	0.075891	11.795	3.7596	1.4832	12.353	11.866	5.0680	14.733
0.29996	0.11319	11.809	4.0091	1.5865	12.406	12.485	5.3514	14.966
0.40006	0.15116	11.821	4.2491	1.6864	12.455	12.980	5.5778	15.168
0.50000	0.18917	11.835	4.5087	1.7951	12.513	13.496	5.8128	15.379
0.60017	0.22737	11.846	4.7537	1.8982	12.564	14.003	6.0425	15.589
0.69943	0.26532	11.859	5.0009	2.0028	12.620	14.504	6.2689	15.802
0.80013	0.30392	11.871	5.4902	2.2114	12.734	15.002	6.4920	16.010
0.90142	0.34285	11.882	6.0004	2.4311	12.859	15.498	6.7133	16.232
1.0001	0.38089	11.898	6.4860	2.6421	12.987	16.019	6.9433	16.464
1.2502	0.47768	11.932	6.9978	2.8665	13.125	16.527	7.1658	16.704
1.5027	0.57605	11.967	7.4807	3.0799	13.257	17.035	7.3859	16.928
1.7492	0.67270	12.003	8.0050	3.3133	13.410	17.540	7.6022	17.159
2.0007	0.77194	12.044	8.4947	3.5328	13.560	18.010	7.8010	17.384
2.2533	0.87223	12.084	8.9943	3.7580	13.715	18.524	8.0161	17.622
2.4933	0.96810	12.123	9.4982	3.9863	13.880	19.017	8.2193	17.860
2.7432	1.0685	12.167	10.001	4.2150	14.051	19.504	8.4175	18.092
2.9997	1.1722	12.210	10.491	4.4386	14.221	19.929	8.5883	18.293
3.2604	1.2783	12.260	10.997	4.6701	14.401			

Table II. (Continued)

p (MPa)	ρ ($\mathrm{mol \cdot L^{-1}}$)	η ($\mu\mathrm{Pa \cdot s}$)	p (MPa)	ρ ($\mathrm{mol \cdot L^{-1}}$)	η ($\mu\mathrm{Pa \cdot s}$)	p (MPa)	ρ ($\mathrm{mol \cdot L^{-1}}$)	η ($\mu\mathrm{Pa \cdot s}$)
$T = 340$ K								
0.09961[a]	0.035271	12.402	4.0016	1.4722	12.978	12.496	4.8641	15.197
0.19776	0.070100	12.421	4.2515	1.5677	13.026	12.972	5.0576	15.356
0.30056	0.10665	12.439	4.4856	1.6575	13.069	13.496	5.2693	15.537
0.40440	0.14365	12.452	4.7412	1.7559	13.121	14.014	5.4785	15.722
0.50192	0.17847	12.461	4.9157	1.8233	13.157	14.501	5.6738	15.895
0.60207	0.21430	12.472	5.5008	2.0506	13.275	15.008	5.8764	16.076
0.70126	0.24986	12.484	5.9913	2.2426	13.380	15.998	6.2689	16.440
0.80271	0.28630	12.496	6.4719	2.4319	13.492	17.022	6.6690	16.826
0.90550	0.32330	12.509	7.0062	2.6436	13.618	17.991	7.0412	17.202
1.0012	0.35780	12.521	7.4843	2.8341	13.737	19.021	7.4295	17.611
1.2635	0.45276	12.558	7.9404	3.0167	13.850	20.086	7.8216	18.039
1.4924	0.53601	12.584	8.0050	3.0426	13.869	20.990	8.1470	18.409
1.7491	0.62982	12.616	8.4914	3.2382	13.996	21.987	8.4973	18.820
1.9944	0.71989	12.654	9.0025	3.4445	14.132	22.949	8.8264	19.219
2.2539	0.81563	12.690	9.4984	3.6453	14.272	23.883	9.1374	19.603
2.4969	0.90570	12.728	9.9907	3.8451	14.414	24.963	9.4865	20.054
2.7526	1.0009	12.763	10.467	4.0389	14.557	25.959	9.7982	20.479
3.0036	1.0948	12.804	10.987	4.2503	14.715	26.947	10.098	20.888
3.2437	1.1850	12.844	11.492	4.4558	14.873	27.799	10.349	21.244
3.5055	1.2838	12.890	11.884	4.6153	14.994	28.767	10.626	21.647
3.7470	1.3753	12.932						

$T = 360$ K								
0.10264	0.034318	12.995	3.7517	1.2891	13.496	12.488	4.4697	15.487
0.19673	0.065830	13.018	3.9987	1.3763	13.539	12.986	4.6522	15.632
0.29873	0.10004	13.032	4.2510	1.4656	13.580	13.481	4.8334	15.778
0.39978	0.13399	13.044	4.5028	1.5550	13.624	13.984	5.0166	15.927
0.50020	0.16778	13.058	4.7519	1.6437	13.672	14.495	5.2022	16.082
0.59990	0.20138	13.067	5.0035	1.7335	13.715	14.994	5.3829	16.241
0.69941	0.23497	13.079	5.5039	1.9128	13.806	16.004	5.7455	16.562
0.79963	0.26885	13.092	6.0066	2.0938	13.906	17.036	6.1114	16.897
0.90023	0.30291	13.100	6.5007	2.2725	14.004	18.016	6.4540	17.222
1.0008	0.33700	13.114	7.0017	2.4544	14.113	18.989	6.7893	17.550
1.2514	0.42222	13.145	7.4960	2.6345	14.217	19.941	7.1116	17.882
1.4991	0.50674	13.176	8.0218	2.8267	14.333	20.983	7.4576	18.248
1.7508	0.59298	13.207	8.5105	3.0058	14.450	21.981	7.7823	18.605
1.9998	0.67856	13.238	8.9786	3.1777	14.561	22.883	8.0697	18.930
2.2471	0.76389	13.275	9.4829	3.3632	14.684	24.023	8.4243	19.328
2.5001	0.85147	13.310	9.9981	3.5529	14.814	24.994	8.7186	19.689
2.7438	0.93612	13.340	10.482	3.7313	14.941	25.975	9.0090	20.052
3.0019	1.0261	13.377	10.993	3.9194	15.076	26.902	9.2764	20.380
3.2510	1.1132	13.416	11.504	4.1078	15.213	28.029	9.5925	20.800
3.5007	1.2008	13.454	11.985	4.2848	15.346	29.183	9.9066	21.225

[a] influenced by slip

Table III. Experimental Viscosity Values of Natural Gas H 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)
$T = 260$ K								
0.09458[a]	0.043890	9.739	3.4924	1.8417	10.587	11.469	8.3444	16.822
0.19919	0.092769	9.762	3.7519	2.0000	10.683	11.993	8.8073	17.472
0.31243	0.14608	9.777	3.9944	2.1511	10.771	12.497	9.2380	18.109
0.40252	0.18879	9.791	4.2426	2.3091	10.864	12.982	9.6354	18.715
0.49850	0.23459	9.812	4.4947	2.4730	10.966	13.482	10.028	19.354
0.60660	0.28654	9.830	4.7421	2.6375	11.066	14.146	10.519	20.248
0.70103	0.33225	9.841	4.9921	2.8073	11.179	14.689	10.896	20.920
0.80040	0.38068	9.863	5.4951	3.1605	11.422	14.994	11.098	21.290
0.89953	0.42934	9.880	5.9963	3.5283	11.692	15.524	11.433	21.931
1.0144	0.48618	9.902	6.5141	3.9253	12.018	15.999	11.717	22.500
1.2500	0.60423	9.953	6.9926	4.3077	12.335	16.668	12.092	23.268
1.5035	0.73351	10.010	7.4902	4.7209	12.706	17.003	12.270	23.643
1.7477	0.86045	10.069	8.0060	5.1649	13.122	17.506	12.525	24.184
1.9987	0.99339	10.132	8.5071	5.6100	13.562	18.025	12.774	24.734
2.2527	1.1306	10.210	9.1921	6.2358	14.250	18.510	12.995	25.255
2.4978	1.2656	10.284	9.5379	6.5570	14.601	19.069	13.237	25.816
2.7652	1.4159	10.372	9.9810	6.9710	15.072	19.508	13.418	26.251
3.0009	1.5511	10.418	10.477	7.4346	15.630	20.016	13.618	26.747
3.2530	1.6987	10.503	10.991	7.9103	16.231			

$T = 280$ K								
0.09614[a]	0.041400	10.404	3.5052	1.6612	11.086	11.491	6.7582	15.428
0.20010	0.086411	10.426	3.7413	1.7855	11.154	11.998	7.1150	15.857
0.30001	0.12990	10.440	3.9968	1.9219	11.232	12.478	7.4501	16.269
0.39794	0.17276	10.453	4.2469	2.0574	11.308	13.011	7.8169	16.740
0.50006	0.21769	10.468	4.4965	2.1946	11.392	13.443	8.1087	17.131
0.60008	0.26194	10.484	4.7441	2.3327	11.477	13.980	8.4644	17.621
0.69977	0.30628	10.494	4.9987	2.4767	11.566	14.544	8.8284	18.192
0.79994	0.35108	10.512	5.4960	2.7641	11.757	15.042	9.1402	18.648
0.89943	0.39582	10.526	5.9902	3.0577	11.964	15.498	9.4176	19.063
1.0014	0.44192	10.545	6.4990	3.3683	12.191	15.972	9.6977	19.479
1.2507	0.55574	10.583	6.9922	3.6773	12.430	16.460	9.9767	19.937
1.5007	0.67148	10.628	7.4928	3.9986	12.687	16.994	10.271	20.431
1.7457	0.78647	10.673	7.9961	4.3291	12.971	17.553	10.567	20.939
1.9974	0.90630	10.722	8.4897	4.6598	13.266	17.997	10.794	21.350
2.2485	1.0275	10.777	9.0313	5.0294	13.609	18.491	11.037	21.789
2.5267	1.1639	10.840	9.4907	5.3476	13.916	19.001	11.279	22.245
2.7604	1.2801	10.894	10.003	5.7061	14.280	19.495	11.504	22.680
2.9982	1.4000	10.951	10.490	6.0496	14.642	20.073	11.757	23.172
3.2471	1.5273	11.016	11.009	6.4175	15.035			

Table III. (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)
$T = 300$ K								
0.10064[a]	0.040430	11.066	3.4988	1.5116	11.682	11.495	5.7739	15.043
0.19961	0.080359	11.088	3.7495	1.6287	11.748	12.001	6.0651	15.354
0.29993	0.12100	11.101	3.9997	1.7468	11.811	12.498	6.3502	15.667
0.40004	0.16173	11.116	4.2457	1.8641	11.874	13.007	6.6404	15.987
0.50001	0.20257	11.131	4.5002	1.9867	11.945	13.503	6.9216	16.318
0.59994	0.24357	11.142	4.7492	2.1079	12.018	14.001	7.2011	16.658
0.69978	0.28470	11.154	5.0011	2.2317	12.097	14.466	7.4590	16.977
0.79936	0.32590	11.170	5.4943	2.4777	12.252	15.000	7.7508	17.350
0.89992	0.36768	11.182	5.9953	2.7323	12.422	15.493	8.0159	17.698
1.0003	0.40958	11.196	6.4989	2.9930	12.604	16.001	8.2838	18.054
1.2501	0.51457	11.236	6.9966	3.2551	12.795	16.508	8.5461	18.425
1.4991	0.62035	11.275	7.4991	3.5241	12.995	17.005	8.7979	18.782
1.7497	0.72795	11.319	8.0013	3.7970	13.215	17.489	9.0374	19.134
1.9983	0.83583	11.365	8.4982	4.0707	13.439	17.975	9.2725	19.493
2.2496	0.94603	11.413	8.9996	4.3502	13.678	18.500	9.5204	19.879
2.4959	1.0552	11.464	9.4946	4.6290	13.924	19.004	9.7516	20.238
2.7460	1.1672	11.506	10.001	4.9168	14.188	19.350	9.9072	20.486
3.0000	1.2822	11.566	10.501	5.2023	14.469	19.851	10.127	20.855
3.2486	1.3959	11.620	10.992	5.4844	14.750			

$T = 320$ K								
0.09842[a]	0.037050	11.717	3.4922	1.3902	12.280	11.500	5.1002	15.046
0.19937	0.075179	11.736	3.7508	1.4994	12.341	12.004	5.3468	15.280
0.30025	0.11341	11.749	3.9996	1.6053	12.400	12.500	5.5888	15.529
0.39586	0.14976	11.767	4.2478	1.7117	12.458	13.000	5.8328	15.777
0.49591	0.18792	11.778	4.4956	1.8187	12.517	13.502	6.0763	16.031
0.60094	0.22812	11.787	4.7466	1.9279	12.577	14.003	6.3180	16.298
0.69910	0.26581	11.799	4.9810	2.0306	12.638	14.497	6.5548	16.560
0.79901	0.30430	11.811	5.4854	2.2538	12.777	14.993	6.7904	16.831
0.90001	0.34334	11.828	5.9916	2.4809	12.924	15.499	7.0283	17.112
1.0003	0.38224	11.841	6.4829	2.7041	13.071	15.997	7.2600	17.395
1.2516	0.48024	11.876	6.9655	2.9259	13.223	16.496	7.4890	17.676
1.4983	0.57728	11.914	7.4970	3.1730	13.404	17.003	7.7186	17.963
1.7503	0.67715	11.954	7.9895	3.4044	13.577	17.496	7.9386	18.263
1.9975	0.77597	11.995	8.4902	3.6418	13.764	17.998	8.1593	18.542
2.2491	0.87734	12.042	9.0047	3.8878	13.962	18.494	8.3733	18.843
2.4981	0.97844	12.088	9.5060	4.1292	14.165	18.996	8.5861	19.136
2.7474	1.0805	12.127	9.9888	4.3630	14.368	19.499	8.7956	19.443
2.9977	1.1838	12.174	10.495	4.6093	14.585	20.002	9.0007	19.731
3.2449	1.2866	12.224	11.005	4.8583	14.816			

[a] influenced by slip

Table IV. Experimental Viscosity Values of Natural Gas L along Isotherms

p (MPa)	ρ $(\mathrm{mol \cdot L^{-1}})$	η $(\mu\mathrm{Pa \cdot s})$	p (MPa)	ρ $(\mathrm{mol \cdot L^{-1}})$	η $(\mu\mathrm{Pa \cdot s})$	p (MPa)	ρ $(\mathrm{mol \cdot L^{-1}})$	η $(\mu\mathrm{Pa \cdot s})$
$T = 260$ K								
0.10238[a]	0.047500	10.410	3.5178	1.8136	11.124	11.623	7.6202	16.177
0.20576	0.095749	10.428	3.7946	1.9741	11.211	12.039	7.9435	16.566
0.30102	0.14047	10.439	3.9956	2.0925	11.270	12.534	8.3225	17.049
0.40886	0.19139	10.454	4.2637	2.2528	11.371	13.060	8.7162	17.574
0.50382	0.23650	10.468	4.5040	2.3989	11.448	13.588	9.1011	18.114
0.63557	0.29951	10.484	4.7950	2.5789	11.564	14.082	9.4499	18.618
0.70151	0.33123	10.491	5.0511	2.7401	11.666	14.583	9.7921	19.113
0.80827	0.38285	10.508	5.5352	3.0521	11.870	15.114	10.142	19.659
0.90525	0.43003	10.520	6.0284	3.3798	12.097	15.581	10.438	20.132
1.0086	0.48062	10.540	6.5379	3.7288	12.353	16.091	10.749	20.639
1.2514	0.60066	10.584	7.0363	4.0802	12.628	16.626	11.061	21.163
1.5006	0.72580	10.622	7.5386	4.4440	12.933	17.111	11.333	21.647
1.7528	0.85434	10.687	8.0202	4.8013	13.232	17.666	11.630	22.167
2.0390	1.0027	10.738	8.5405	5.1958	13.595	18.186	11.896	22.652
2.2553	1.1166	10.789	9.0735	5.6075	13.983	18.674	12.135	23.116
2.5513	1.2750	10.857	9.5759	6.0012	14.376	19.180	12.373	23.572
2.7509	1.3835	10.909	10.087	6.4051	14.797	19.682	12.599	24.030
2.9993	1.5205	10.973	10.545	6.7685	15.173	20.227	12.834	24.513
3.2659	1.6700	11.043	11.062	7.1789	15.647			

$T = 280$ K								
0.09502[a]	0.040900	11.094	3.5011	1.6300	11.762	11.480	6.2838	15.402
0.19870	0.085732	11.120	3.7404	1.7512	11.828	11.974	6.5936	15.733
0.30073	0.13005	11.138	4.0049	1.8867	11.898	12.476	6.9076	16.067
0.39998	0.17336	11.152	4.2457	2.0114	11.968	12.988	7.2249	16.426
0.50196	0.21806	11.166	4.5038	2.1466	12.043	13.482	7.5276	16.782
0.60214	0.26217	11.177	4.7497	2.2768	12.119	13.982	7.8303	17.153
0.70630	0.30825	11.190	5.0050	2.4135	12.204	14.484	8.1297	17.526
0.80531	0.35225	11.206	5.5029	2.6843	12.375	14.986	8.4232	17.903
0.90365	0.39615	11.222	5.9838	2.9512	12.547	15.473	8.7026	18.255
1.0011	0.43986	11.238	6.4885	3.2368	12.746	15.969	8.9809	18.639
1.2547	0.55447	11.282	6.9886	3.5251	12.952	16.480	9.2609	19.024
1.5108	0.67159	11.326	7.4884	3.8183	13.172	16.975	9.5257	19.402
1.7510	0.78265	11.373	8.0003	4.1235	13.415	17.477	9.7867	19.786
1.9984	0.89836	11.420	8.4767	4.4116	13.646	17.981	10.042	20.172
2.2557	1.0201	11.473	9.0066	4.7360	13.924	18.469	10.282	20.541
2.4979	1.1360	11.524	9.4845	5.0317	14.190	18.976	10.524	20.933
2.7524	1.2592	11.580	9.9733	5.3365	14.465	19.505	10.769	21.334
3.0145	1.3876	11.634	10.469	5.6471	14.764	19.999	10.991	21.701
3.2503	1.5044	11.695	10.982	5.9703	15.081			

Table IV. (Continued)

p (MPa)	ρ ($\mathrm{mol \cdot L^{-1}}$)	η ($\mu\mathrm{Pa \cdot s}$)	p (MPa)	ρ ($\mathrm{mol \cdot L^{-1}}$)	η ($\mu\mathrm{Pa \cdot s}$)	p (MPa)	ρ ($\mathrm{mol \cdot L^{-1}}$)	η ($\mu\mathrm{Pa \cdot s}$)
$T = 300$ K								
0.12266[a]	0.049280	11.814	3.5301	1.5050	12.412	11.511	5.4944	15.350
0.21136	0.085050	11.829	3.7485	1.6041	12.462	12.007	5.7554	15.599
0.30434	0.12266	11.845	3.9987	1.7185	12.523	12.498	6.0136	15.858
0.40358	0.16294	11.858	4.2536	1.8360	12.584	12.999	6.2757	16.119
0.50343	0.20361	11.872	4.5166	1.9582	12.652	13.489	6.5308	16.393
0.60682	0.24587	11.887	4.7503	2.0676	12.719	13.997	6.7934	16.669
0.71863	0.29174	11.898	4.9976	2.1842	12.785	14.494	7.0479	16.950
0.81950	0.33328	11.912	5.4907	2.4193	12.929	14.996	7.3024	17.233
0.90316	0.36784	11.922	5.9918	2.6616	13.079	15.495	7.5520	17.520
1.0157	0.41451	11.940	6.4941	2.9077	13.243	15.991	7.7973	17.806
1.2616	0.51704	11.981	6.9862	3.1519	13.413	16.503	8.0464	18.115
1.5076	0.62053	12.027	7.4938	3.4067	13.594	17.013	8.2906	18.426
1.7553	0.72563	12.062	8.0127	3.6700	13.784	17.493	8.5164	18.708
2.0023	0.83133	12.110	8.4904	3.9147	13.982	18.000	8.7508	19.025
2.2599	0.94250	12.150	8.9864	4.1708	14.182	18.488	8.9723	19.325
2.5382	1.0637	12.206	9.4916	4.4335	14.394	18.990	9.1954	19.635
2.7574	1.1600	12.242	9.9872	4.6927	14.618	19.506	9.4201	19.955
3.0032	1.2688	12.298	10.486	4.9544	14.846	20.007	9.6334	20.261
3.2544	1.3809	12.354	11.000	5.2254	15.098			

$T = 320$ K								
0.10845[a]	0.040820	12.486	3.5273	1.3893	13.032	11.549	4.9298	15.497
0.20922	0.078861	12.506	3.7526	1.4823	13.080	11.992	5.1320	15.676
0.30618	0.11556	12.516	4.0027	1.5861	13.137	12.550	5.3865	15.900
0.42386	0.16023	12.530	4.2476	1.6883	13.183	12.995	5.5891	16.100
0.53551	0.20274	12.549	4.4973	1.7931	13.242	13.505	5.8198	16.327
0.60535	0.22940	12.552	4.7523	1.9007	13.306	13.989	6.0380	16.541
0.69886	0.26517	12.562	4.9955	2.0039	13.358	14.492	6.2633	16.767
0.81150	0.30838	12.582	5.5103	2.2240	13.489	14.989	6.4847	16.998
0.90353	0.34378	12.594	6.0136	2.4414	13.620	15.493	6.7067	17.234
0.99958	0.38082	12.602	6.5002	2.6535	13.750	16.000	6.9287	17.478
1.2525	0.47882	12.642	6.9821	2.8653	13.893	16.491	7.1410	17.716
1.5046	0.57711	12.680	7.5044	3.0967	14.054	16.995	7.3565	17.957
1.7479	0.67262	12.714	8.0138	3.3240	14.211	17.525	7.5807	18.227
2.0046	0.77404	12.756	8.4864	3.5362	14.365	18.010	7.7827	18.459
2.2513	0.87216	12.802	8.9933	3.7650	14.539	18.568	8.0122	18.742
2.5190	0.97932	12.844	9.5102	3.9994	14.718	19.004	8.1888	18.965
2.7870	1.0873	12.892	10.062	4.2505	14.920	19.523	8.3961	19.229
3.0004	1.1738	12.934	10.478	4.4404	15.079	20.013	8.5889	19.485
3.2939	1.2935	12.983	11.009	4.6830	15.281			

[a] influenced by slip

The reproducibility of the measurements on methane was within ±0.02% at pressures up to 1 MPa and within ±0.05% at pressures up to 20 and 29 MPa. But the reproducibility for the natural gases was found to increase to ±0.2% over the complete pressure range. The uncertainty for the measurements on methane is conservatively estimated to be ±0.3% [9], whereas that for the measurements on the natural gas specimens is assumed to be ±0.5% considering the retrograde behavior and the effects of adsorption and desorption [10].

The experimental results of each isotherm for methane and for the natural gas samples were correlated as a function of the molar density by means of a power series restricted to the fourth or a lower power depending on the density range considered.

$$\eta(T,\rho)=\eta^{(0)}(T)+\eta^{(1)}(T)\,\rho+\eta^{(2)}(T)\,\rho^2+\eta^{(3)}(T)\,\rho^3+\eta^{(4)}(T)\,\rho^4. \qquad (1)$$

Weighting factors of η^{-2} were used in the multiple linear least-squares regression to minimize the relative deviations. The coefficients are given in Table V for methane and both natural gases.

Table V. Coefficients of Eq. (1)

T (K)	$\rho_{\max}$ (mol$\cdot$L^{-1})	$\eta^{(0)}$ (μPa$\cdot$s)	$\eta^{(1)}\times10^3$ (μPa$\cdot$s$\cdot$L$\cdot$mol^{-1})	$\eta^{(2)}\times10^3$ (μPa$\cdot$s$\cdot$L$^2\cdot$mol^{-2})	$\eta^{(3)}\times10^3$ (μPa$\cdot$s$\cdot$L$^3\cdot$mol^{-3})	$\eta^{(4)}\times10^3$ (μPa$\cdot$s$\cdot$L$^4\cdot$mol^{-4})	σ (%)
Methane							
260	12.8	9.812	268.7	68.13	−2.435	0.1257	0.021
280	11.0	10.483	281.9	67.26	−2.479	0.1270	0.019
300	9.7	11.139	291.6	65.85	−2.454	0.1285	0.013
320	8.6	11.773	300.5	65.89	−2.788	0.1558	0.015
340	10.6	12.405	295.6	68.38	−3.060	0.1611	0.016
360	9.9	13.003	304.2	65.55	−2.700	0.1453	0.017
H natural gas							
260	13.6	9.723	353.1	63.39	−1.448	0.1197	0.084
280	11.8	10.399	291.5	78.30	−2.635	0.1470	0.048
300	10.1	11.065	291.1	83.13	−3.571	0.1926	0.020
320	9.0	11.715	297.1	85.22	−4.238	0.2339	0.022
L natural gas							
260	12.8	10.397	267.5	77.73	−2.843	0.1433	0.033
280	11.0	11.096	295.2	73.48	−2.711	0.1426	0.021
300	9.6	11.809	288.7	80.21	−3.974	0.2064	0.026
320	8.6	12.482	296.5	77.86	−3.915	0.2190	0.019

4. CORRELATION AND PREDICTION OF THE VISCOSITY OF NATURAL GAS

The viscosity $\eta(\rho, T, x)$ of a gas mixture at molar density ρ, temperature T and composition x may be composed of two contributions which can be analyzed independently.

$$\eta(\rho, T, x) = \eta^{(0)}(T, x) + \Delta\eta(\rho_\mathrm{r}, x). \tag{2}$$

The viscosity in the limit of zero density $\eta^{(0)}$ is given as a function of temperature T and gas composition x, whereas the residual part of the viscosity $\Delta\eta$ has been considered to be a function of only the reduced molar density ρ_r and composition x.

The viscosity in the limit of zero density $\eta^{(0)}$ for a gas mixture is given according to Wilke [14] by

$$\eta^{(0)}(T, x) = \sum_{i=1}^{n} \frac{x_i \eta_i^{(0)}(T)}{\sum_{j=1}^{n} x_j \phi_{ij}}, \tag{3}$$

$$\phi_{ij} = \frac{[1 + (\eta_i^{(0)}/\eta_j^{(0)})^{1/2} (M_j/M_i)^{1/4}]^2}{[8\,(1 + M_i/M_j)]^{1/2}}. \tag{4}$$

Here $\eta_i^{(0)}(T)$ is the viscosity in the limit of zero density for the individual pure component i, x_i is the molar fraction, M_i is the molar mass of component i, and ϕ_{ij} is the interaction parameter given by the mixing rule of Wilke.

The composition analysis of the two natural gases (see Table I) shows that, in principle, the zero-density viscosity of 21 components is needed to predict the viscosity of natural gas mixtures. On the other hand, the mole fraction of some components is very small and their contribution to the viscosity of a natural gas mixture is insignificant. Therefore, the number of components considered for the prediction of the zero-density viscosity of natural gas has been reduced to 12: methane (+ hydrogen), nitrogen (+ helium + oxygen/argon), carbon dioxide, ethane, propane, n-butane, isobutane, n-pentane (+ benzene), isopentane (+ neopentane), n-hexane (hexanes + toluene), n-heptane (heptanes), and n-octane (octanes + nonanes+ C_{10} plus higher + xylenes).

The residual part of the viscosity $\Delta\eta(\rho_\mathrm{r}, x)$ is given as

$$\Delta\eta(\rho_\mathrm{r}, x) = \eta_{\mathrm{c,mix}}(x)\, \Delta\eta_\mathrm{r}(\rho_\mathrm{r}). \tag{5}$$

Here, the factor $\eta_{\mathrm{c,mix}}$ is used to obtain a dimensionless residual viscosity $\Delta\eta_\mathrm{r}(\rho_\mathrm{r})$. In contrast to thermodynamic properties, a *critical* value of the viscosity cannot be used as a reducing parameter, since its derivation from the so-called background contribution is connected with a large uncertainty due to the experimental scatter. To deduce a reliable and characteristic value for the composition dependence of the viscosity of a mixture the factor was chosen to be

$$\eta_{\mathrm{c,mix}}(x)=\frac{(M_{\mathrm{mix}})^{1/2}(p_{\mathrm{c,mix}})^{2/3}}{R^{1/6}N_{\mathrm{A}}^{1/3}(T_{\mathrm{c,mix}})^{1/6}}, \tag{6}$$

where R is the universal gas constant, and N_{A} is Avogadro's number. The pseudo-critical properties for the mixture $T_{\mathrm{c,mix}}$, $V_{\mathrm{c,mix}}$, $Z_{\mathrm{c,mix}}$ are summed up from the critical properties of the pure components leading to the pseudo-critical pressure $p_{\mathrm{c,mix}}$ of the mixture.

$$T_{\mathrm{c,mix}}=\sum_{i=1}^{n}x_i T_{\mathrm{c},i}, \qquad V_{\mathrm{c,mix}}=\sum_{i=1}^{n}x_i V_{\mathrm{c},i}, \tag{7}$$

$$Z_{\mathrm{c},i}=\frac{p_{\mathrm{c},i}V_{\mathrm{c},i}}{RT_{\mathrm{c},i}}, \qquad Z_{\mathrm{c,mix}}=\sum_{i=1}^{n}x_i Z_{\mathrm{c},i}, \qquad p_{\mathrm{c,mix}}=\frac{Z_{\mathrm{c,mix}}\,R\,T_{\mathrm{c,mix}}}{V_{\mathrm{c,mix}}}. \tag{8}$$

The reduced density ρ_{r} and the critical density of the mixture $\rho_{\mathrm{c,mix}}$ follow from the molar mass M_{mix} and the critical volume $V_{\mathrm{c,mix}}$.

$$\rho_{\mathrm{r}}=\frac{\rho(p,T,x)}{\rho_{\mathrm{c,mix}}}, \qquad \rho_{\mathrm{c,mix}}=\frac{M_{\mathrm{mix}}}{V_{\mathrm{c,mix}}}, \qquad M_{\mathrm{mix}}=\sum_{i=1}^{n}x_i M_i. \tag{9}$$

The density dependence of the dimensionless residual part of the viscosity $\Delta\eta_{\mathrm{r}}(\rho_{\mathrm{r}})$ has been derived by fitting it to the experimental data of methane of this paper only and using

$$\eta_{\mathrm{c,CH_4}}=\frac{(M_{\mathrm{CH_4}})^{1/2}(p_{\mathrm{c,CH_4}})^{2/3}}{R^{1/6}N_{\mathrm{A}}^{1/3}(T_{\mathrm{c,CH_4}})^{1/6}}. \tag{10}$$

As the temperature range of the experimental data (260–360 K) is rather limited, the temperature dependence of the dimensionless residual part of the viscosity has been neglected.

4.1. Prediction of the Zero-Density Viscosity of Natural Gas

In principle, the temperature function $\eta_i^{(0)}(T)$ of the viscosity in the limit of zero density of a pure polyatomic gas i can adequately be represented by the kinetic theory of dilute monatomic gases. The procedure described for methane in Ref. [9] uses in a first step a universal correlation for the monatomics (Bich et al. [15]). In a second step the incomplete knowledge concerning the intermolecular potential energy surface is taken into account using an individual correlation. Individual correlations for the greatest possible temperature range of the zero-density viscosity have been derived for seven of the twelve pure components considered: methane [9], nitrogen [16], carbon dioxide [17], ethane [18], propane [19], n-butane [20], and isobutane [21]. Unfortunately, viscosity values at such low temperatures needed for the natural gas mixtures could not be included in the derivation of the individual correlations for the last three of the seven components. The data situation is even worse for the remaining five components so that an extrapolation to low temperatures is necessary for most of the 12 components.

Consequently, for the limited temperature range of application (250–450 K) a simpler approach using a quadratic or cubic equation should be appropriate for the extrapolation to lower temperatures

$$\eta_i^{(0)}(T) = \eta_{0,i}^{(0)}\left[1.0 + a_{1,i}(T - T_0) + a_{2,i}(T - T_0)^2 + a_{3,i}(T - T_0)^3\right], \quad (11)$$

where $\eta_{0,i}^{(0)}$ is the viscosity at $T_0 = 273.15$ K. The values of $\eta_{0,i}^{(0)}$, $a_{1,i}$, $a_{2,i}$, and $a_{3,i}$ were determined using viscosity values obtained by extrapolation to zero density or values at very low densities. Most of the measurements were performed in our laboratory by means of an oscillating-disk viscometer or the vibrating-wire viscometer used in this paper. Information about the experimental data sources used in this work is provided in Table VI. The coefficients are listed for the 12 individual components in Table VII.

The results for the representation of the zero-density viscosity with Eq. (11) for the four main components of the natural gas mixtures are illustrated in Fig. 1. The weights of the experimental data of other research groups at low temperatures were chosen to be so small that, in principle, they do not influence the results of the fit. Nevertheless, the data, particularly those of Smith and co-workers [23,24,27,28,30,31] are represented within ±0.5% down to 200 K corresponding to the upper limit of the assumed experimental uncertainty. Furthermore, in the case of nitrogen and carbon dioxide the cubic form of Eq. (11) had to be used. Near 200 K deviations of −2.2% for nitrogen [23,24] and of +0.9% for carbon dioxide [30] were obtained with the quadratic form. Such large deviations are due to the chosen form of the fitting equation. A comparison with values based on the individual correlations for nitrogen [16] and carbon dioxide [17] as well as with values calculated from the intermolecular potential energy hypersurfaces using the classical trajectory approach for nitrogen [40] and carbon

Table VI. Experimental Data Sources for the Viscosity of the Pure Components in the Limit of Zero Density

Component i	Reference	Experimental uncertainty (%)	Temperature range (K)	No. of points	Weight in fit of Eq. (11)
Methane	This work	0.2–0.3	260–360	6	1
	Johnston, McCloskey [22]	1.0	200–300	8	0.01
	Clarke, Smith [23]	1.0–0.5	200–299	4	0.01
	Gough et al. [24]	1.0–0.5	200–300	6	0.01
	Kestin et al. [25]	0.2–0.7	296–474	7	0.01
Nitrogen	Vogel [26]	0.15–0.3	297–640	10	1 (0.2[a])
	Vogel et al. [16]	0.15–0.3	299–689	15	1 (0.2[a])
	Seibt, Vogel et al.	0.2–0.3	298–423	6	1
	Clarke, Smith [27]	1.0–0.5	200–299	5	0.01
	Matthews et al. [28]	1.0–0.5	204–298	4	0.01
Carbon dioxide	Hendl et al. [29]	0.15–0.3	297–625	13	1 (0.2[a])
	Harris et al. [30]	1.0–0.5	203–293	8	0.01
	Hunter et al. [31]	1.0–0.5	213–301	5	0.01
Ethane	Hendl, Vogel [32]	0.15–0.3	293–633	12	1 (0.2[a])
	Wilhelm, Vogel et al.	0.2–0.3	290–430	8	1
	Meshcheryakov, Golubev [33]	1.0	258–294	3	0.01
	Hunter, Smith (Pers. Commun)	1.0–0.5	212–252	4	0.01
Propane	Vogel [34]	0.15–0.3	297–625	14	1
	Wilhelm, Vogel [8]	0.2–0.3	298-423	7	1
n-Butane	Küchenmeister, Vogel [35]	0.15–0.3	298–626	14	1
Isobutane	Küchenmeister, Vogel [36]	0.15–0.3	298–627	14	1
n-Pentane	Vogel, Holdt [37]	0.15–0.3	299–632	7+14[b]	1
Isopentane	Golubev, Gnezdilov [38]	1.0	260–360	10	1
n-Hexane	Vogel, Strehlow [39]	0.15–0.3	299–630	9+14[b]	1
n-Heptane	Vogel, Holdt [37]	0.15–0.3	318–632	7+14[b]	1
n-Octane	Golubev, Gnezdilov [38]	1.0	260–360	8	1

[a] weight for $T > 500$ K.

[b] series at the lowest density.

Table VII. Coefficients for the Representation of the Zero-Density Viscosity of Pure Components using Eq. (11)

Component i	$\eta_{0,i}^{(0)}$ (μPa·s)	$a_{1,i}$ (10^{-3} K^{-1})	$a_{2,i}$ (10^{-6} K^{-2})	$a_{3,i}$ (10^{-9} K^{-3})
Methane	10.257	3.230	−1.613	0.0
Nitrogen	16.627	2.848	−1.940	1.372
Carbon dioxide	13.717	3.539	−1.007	−0.443
Ethane	8.487	3.607	−1.319	0.0
Propane	7.461	3.669	−1.052	0.0
n-Butane	6.814	3.613	−0.494	0.0
Isobutane	6.914	3.515	−0.682	0.0
n-Pentane	6.196	3.759	−0.698	0.0
Isopentane	6.384	3.531	−0.376	0.0
n-Hexane	5.735	3.731	−0.479	0.0
n-Heptane	5.335	3.732	−0.277	0.0
n-Octane	5.095	3.854	−0.014	0.0

dioxide [17] shows also that, in fact, the uncertainty of the experimental data by Smith and co-workers is reasonably assessed. On the other hand, the quadratic form of Eq. (11) has resulted in a satisfactory representation in the case of ethane. Hence, this form was chosen for all other substances because no low temperature data are available.

The results predicted for the zero-density viscosity of the natural gases H and L using the Wilke formalism according to Eqs. (3) and (4) can be seen in Fig. 2 for $p \to 0$. The predicted values agree for both natural gases within ±0.3% with the values derived from the experimental data. This demonstrates that for a limited temperature range of application (250–450 K) the zero-density correlations using Eq. (11) are appropriate for a reasonably small extrapolation to lower temperatures necessary for a number of the natural gas components.

4.2. Prediction of the Residual Viscosity of Natural Gas

As already mentioned above, the density dependence of the dimensionless residual viscosity $\Delta\eta_r(\rho_r)$ has been deduced by fitting to only the experimental methane data of this paper. The following polynomial in the reduced density ρ_r has been used

$$\Delta\eta_r(\rho_r) = \sum_{j=1}^{4} c_j \rho_r^j. \tag{12}$$

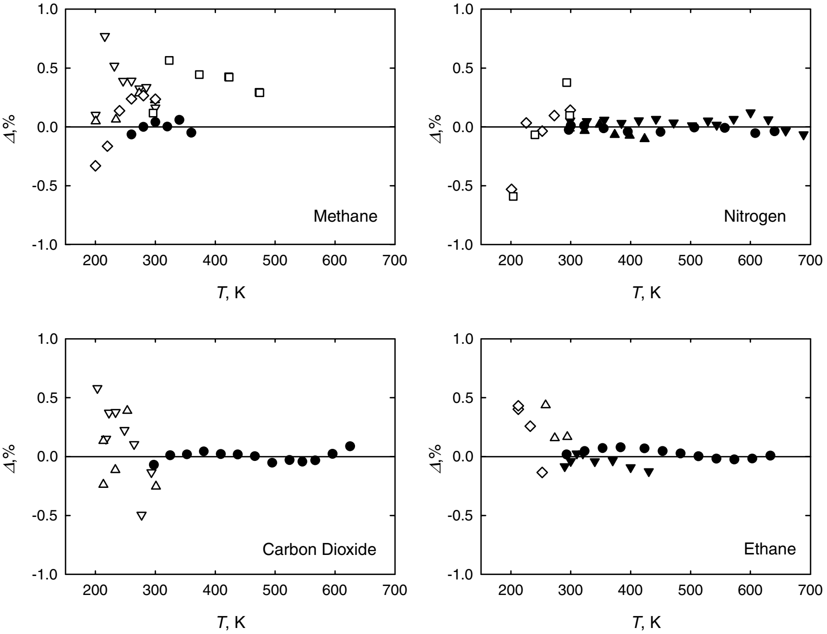

Fig. 1. Comparison of experimental zero-density viscosity data for methane, nitrogen, carbon dioxide, and ethane with viscosity values calculated with Eq. (11). Deviations $[\Delta = 100(\eta_{\mathrm{exp}}^{(0)} - \eta_{\mathrm{cal}}^{(0)})/\eta_{\mathrm{cal}}^{(0)}]$ as a function of temperature. Experimental data for methane: (●) present work, (▽) Johnston and McCloskey [22], (△) Clarke and Smith [23], (◇) Gough et al. [24], (□) Kestin et al. [25]. Experimental data for nitrogen: (●) Vogel [26], (▼) Vogel et al. [16], (▲) Seibt, Vogel et al. (◇) Clarke and Smith [27], (□) Matthews et al. [28]. Experimental data for carbon dioxide: (●) Hendl et al. [29], (▽) Harris et al. [30], (△) Hunter et al. [31]. Experimental data for ethane: (●) Hendl and Vogel [32], (▼) Wilhelm, Vogel et al. (△) Meshcheryakov and Golubev [33], (◇) Hunter and Smith.

The coefficients obtained are listed in Table VIII. The results of the fit are shown in Fig. 2 for the total viscosity value $\eta(T, p)$ of methane. The deviations between the experimental data and the correlated values are within ±0.5% demonstrating that the temperature dependence of the residual viscosity is negligible within this limit considering the temperature range of application.

The critical constants T_{c}, V_{c}, and p_{c} needed to calculate the pseudocritical viscosity values η_{c} [Eq. (6)] for the composition dependence of the residual viscosity have been taken from a compilation given by Span and Wagner [41] and the constants for isopentane by Das et al. [42]. All the constants are summarized in Table VIII for convenient use together with the η_{c} values for methane and both natural gases. Finally, the viscosities for the two natural gases have been calculated using Eqs. (2), (5)–(10), and

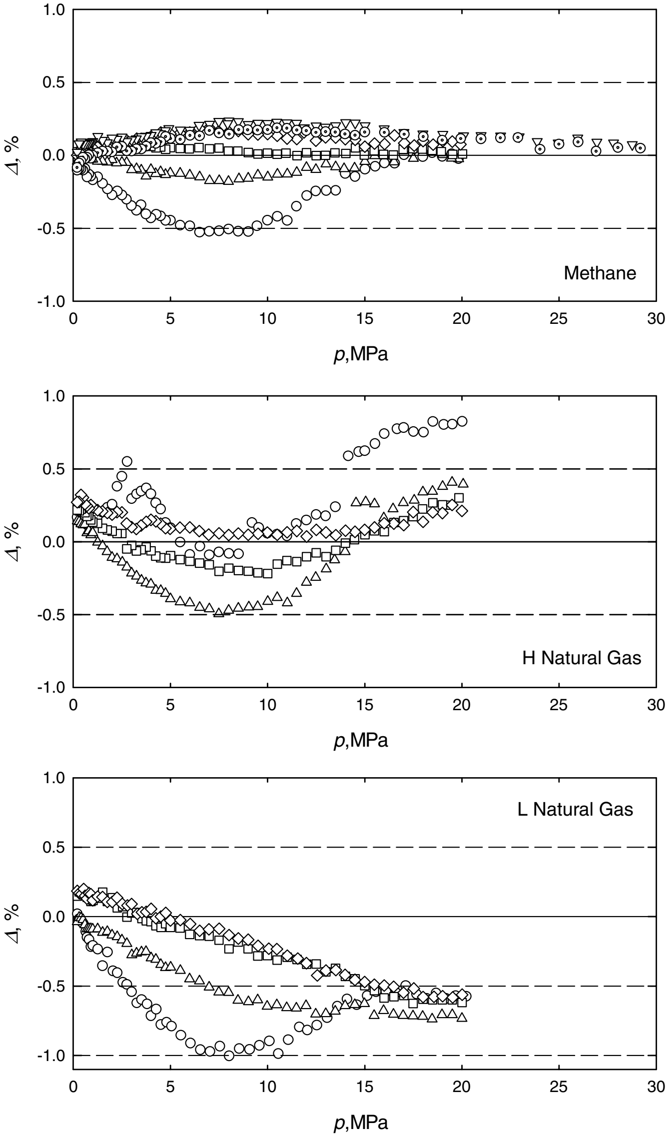

Fig. 2. Deviations $[\Delta = 100(\eta_{\mathrm{exp}} - \eta_{\mathrm{cal}})/\eta_{\mathrm{cal}}]$ of experimental viscosity data of methane, of H natural gas, and of L natural gas from correlated values according to Eqs. (2), (5)–(10) and (12). (○) 260 K, (△) 280 K, (□) 300 K, (◇) 320 K, (▽) 340 K, (⊙) 360 K.

Table VIII. Coefficients and Constants for the Representation of the Residual Viscosity

Eq. (12)	c_1	c_2	c_3	c_4	
Eqs. (5)–(10)	0.23961032	0.57790957	−0.24327596	0.12776597	
Component i	M_i $(\mathrm{kg \cdot kmol^{-1}})$	$T_{c,i}$ (K)	$10^3 \times V_{c,i}$ $(\mathrm{L \cdot mol^{-1}})$	$p_{c,i}$ (MPa)	$\eta_{c,i}$ $(\mu\mathrm{Pa \cdot s})$
Methane	16.043	190.564	98.63	4.599	12.149
Nitrogen	28.0135	126.192	89.41	3.396	
Carbon dioxide	44.010	304.1282	94.12	7.377	
Ethane	30.070	305.322	145.55	4.872	
Propane	44.097	369.825	200.00	4.248	
n-Butane	58.123	425.125	255.10	3.796	
Isobutane	58.123	407.817	259.06	3.640	
n-Pentane	72.150	469.70	310.99	3.370	
Isopentane	72.150	460.35	305.72	3.396	
n-Hexane	86.177	507.82	369.57	3.034	
n-Heptane	100.204	540.13	431.91	2.736	
n-Octane	114.231	569.32	486.30	2.497	
Mixtures	M_i $(\mathrm{kg \cdot kmol^{-1}})$	$T_{c,\mathrm{mix}}$ (K)	$(\mathrm{L \cdot mol^{-1}})$	$p_{c,\mathrm{mix}}$ (MPa)	$\eta_{c,\mathrm{mix}}$ $(\mu\mathrm{Pa \cdot s})$
Natural gas H	17.993	201.38	103.85	4.605	12.758
Natural gas L	18.468	191.94	100.66	4.536	12.899

(12). Figure 2 shows that the maximum difference between the experimental and predicted viscosities is ±1% over the entire investigated temperature and pressure ranges.

5. CONCLUSIONS

A vibrating-wire viscometer of very high precision at the University of Rostock was used to measure the viscosity coefficient of methane and of two natural gases. The estimated uncertainties are ±0.3 and ±0.5% for methane and the natural gases, respectively.

The new experimental data for methane were used together with literature data to develop a viscosity equation for natural gas. It is composed of two contributions analyzed independently. The zero-density viscosity part, given as a function of temperature and composition, uses the mixing rule of Wilke [14]. The zero-density viscosity correlations needed for the pure components methane, nitrogen, carbon dioxide, ethane, propane, n- and isobutane, n- and isopentane, n-hexane, n-heptane, and n-octane were deduced from experimental values of this study and some literature data using a simple quadratic or cubic equation. The density dependence of the residual viscosity part was correlated with methane data only, neglecting any temperature dependence, whereas the composition dependence is characterized by a pseudo-critical viscosity value. For methane the agreement between the correlated and experimental data is within ±0.5%. The values predicted with the correlation and the experimental data agree within ±1% for both the high calorific, H, natural gas and the low calorific, L, natural gas.

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