

Viscosity Measurements on Methanol Vapor and Their Evaluation

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The viscosity coefficient of methanol vapor was measured at low densities by means of an all-quartz oscillating-disk viscometer of high precision. The relative measurements were performed along 10 isochores at densities from (0.004 to 0.050) mol·dm⁻³ in the temperature range between (298 and 603) K. The uncertainty is estimated to be ± 0.2 % at room temperature, increasing up to ± 0.3 % at higher temperatures. Isothermal values recalculated from the original experimental data were evaluated with a first-order expansion for the viscosity in terms of density. A reasonable agreement with experimental values from the literature was found for those of Golubev and Likhachev (up to 1 % higher) measured with a capillary viscometer in an extended temperature range up to high pressures. The new results, some older ones obtained in our laboratory, and those of Golubev and Likhachev are used to model the viscosity of methanol vapor at moderately low densities. Whereas an individual correlation according to the extended theorem of corresponding states was necessary to represent the zero-density viscosity coefficient within its uncertainty, the Rainwater–Friend theory proved to be suitable for the description of the second viscosity virial coefficient. In addition, viscosity values of the saturated vapor were determined at low temperatures (299 to 339 K). They are in reasonable good consistency with values of Golubev determined at higher temperatures (373 to 513 K).

Introduction

Since the 1960s, the Division of Physical Chemistry of the International Union of Pure and Applied Chemistry, in particular the Commission on Thermodynamics, has devoted considerable efforts to the development of internationally agreed tables and formulations concerning the thermodynamic properties of a number of fluids of industrial and scientific importance. Hence in 1993, de Reuck and Craven¹ published a formulation of the thermodynamic properties of methanol, which belongs to the most important bulk chemicals and has frequently been investigated. But the corresponding transport property surfaces have not been derived until now due to the fact that these properties have not been measured with the same thoroughness. The development of such correlations requires reliable experimental values of high precision in extended ranges of temperature as well as pressure and density, respectively. Equations for limited ranges, in particular at atmospheric pressure and for the liquid at higher pressures, were reported by Zubarev et al.² in 1973 (see also Vargaftik et al.³).

With respect to the development of the viscosity surface of methanol over a wide range of thermodynamic states, the corresponding correlation should be based on the residual viscosity concept given as a function of temperature (T) and molar density (ρ) by

$$\eta(T, \rho) = \eta^{(0)}(T) + \eta^{(1)}(T) \rho + \Delta\eta_h(T, \rho) + \Delta\eta_c(T, \rho) \quad (1)$$

Here, $\eta^{(0)}$ and $\eta^{(1)}$ are the viscosity coefficients in the limit of zero-density and of the initial-density dependence. $\Delta\eta_h$ is the residual contribution that considers the effect of increasing density outside the critical region. Finally, $\Delta\eta_c$ is the critical enhancement of the viscosity arising from long-range fluctuations. A theoretically based correlation scheme should start in the region of the moderately dense gas taking into account $\eta^{(0)}$

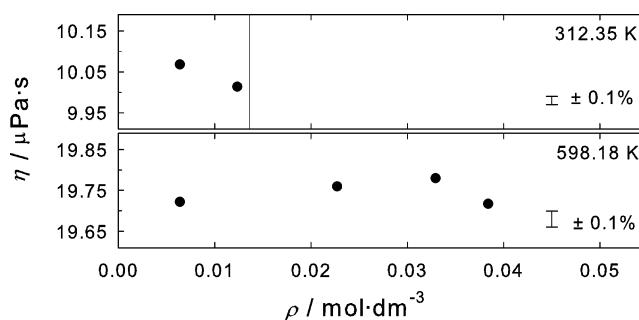


Figure 1. Measurements of the viscosity of methanol vapor as a function of molar density performed by Vogel et al.⁴ ●, quasi-experimental values.

and $\eta^{(1)}$. But measurements at very low densities or even in the limit of zero density are not feasible so that $\eta^{(0)}$ and $\eta^{(1)}$ are derived from isotherms with a sufficient number of experimental points at moderately low densities. The slope of the isotherms corresponds to the initial-density viscosity coefficient ($\eta^{(1)}$), their value extrapolated to the limit of zero density is $\eta^{(0)}$.

An inspection of the open literature revealed that only a limited number of experimental viscosity data, mostly of comparably large uncertainty, are available for methanol vapor at moderate density. The present measurements on methanol vapor have been intended to provide reliable experimental viscosity values in a temperature range as large as possible but is restricted to moderately low densities.

Nearly 20 years ago, Vogel et al.⁴ performed measurements on methanol vapor in our laboratory. The results of this investigation suffered in that only five isochoric series of measurements were carried out at comparably low densities and that a decomposition or a reversible reaction could have affected the evaluation of the experimental data at higher temperatures. The problems of this investigation are demonstrated in Figure 1 for the lowest and highest isotherms of the quasi-experimental values derived from the original isochoric data. For the 312 K isotherm, only two points could be included in the evaluation since the limit of the saturated vapor is very low as marked as

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Table 1. Viscosity of Methanol Vapor

<i>T</i>	η	<i>T</i>	η	<i>T</i>	η	<i>T</i>	η	<i>T</i>	η
K	$\mu\text{Pa}\cdot\text{s}$	K	$\mu\text{Pa}\cdot\text{s}$	K	$\mu\text{Pa}\cdot\text{s}$	K	$\mu\text{Pa}\cdot\text{s}$	K	$\mu\text{Pa}\cdot\text{s}$
series 1		series 2		series 3		series 4		series 5	
$\rho = 0.00379 \text{ mol}\cdot\text{dm}^{-3}$		$\rho = 0.00632 \text{ mol}\cdot\text{dm}^{-3}$		$\rho = 0.00817 \text{ mol}\cdot\text{dm}^{-3}$		$\rho = 0.01010 \text{ mol}\cdot\text{dm}^{-3}$		$\rho = 0.01320 \text{ mol}\cdot\text{dm}^{-3}$	
297.64	9.594	298.16	9.594	297.43	9.551	297.41	9.532	298.54	9.579
312.54	10.098	312.25	10.076	311.23	10.023	313.89	10.084	314.18	10.076
324.75	10.504	325.91	10.544	325.15	10.502	325.22	10.496	325.76	10.488
338.69	10.977	339.77	11.007	338.47	10.951	338.62	10.942	339.34	10.957
352.93	11.444	355.50	11.520	352.62	11.434	352.86	11.425	353.26	11.432
366.84	11.914	367.84	11.949	366.82	11.910	366.59	11.892	367.10	11.894
381.27	12.396	382.15	12.438	381.38	12.405	380.86	12.381	380.97	12.361
395.39	12.872	396.23	12.908	394.76	12.857	394.63	12.854	395.40	12.853
411.30	13.430	411.31	13.425	412.33	13.460	409.51	13.362	409.39	13.331
423.50	13.828	424.73	13.883	423.31	13.821	423.96	13.852	423.77	13.826
440.61	14.412	440.07	14.406	437.81	14.312	437.60	14.314	438.41	14.318
468.85	15.365		<i>a</i>		<i>b</i>	467.33	15.302	467.74	15.310
496.65	16.308			496.40	16.275	496.56	16.289	496.43	16.273
525.41	17.267			525.42	17.265		<i>a</i>	526.39	17.286
547.13	18.020			546.79	18.001		<i>b</i>	546.84	17.978
569.26	18.787							567.40	18.684
597.60	19.772			602.56	19.937			596.93	19.693
352.91	11.478	353.30	11.480	353.05	11.457	353.44	11.471	353.22	11.435
series 6		series 7		series 8		series 9		series 10	
$\rho = 0.01793 \text{ mol}\cdot\text{dm}^{-3}$		$\rho = 0.02458 \text{ mol}\cdot\text{dm}^{-3}$		$\rho = 0.03222 \text{ mol}\cdot\text{dm}^{-3}$		$\rho = 0.03868 \text{ mol}\cdot\text{dm}^{-3}$		$\rho = 0.04953 \text{ mol}\cdot\text{dm}^{-3}$	
301.53	9.672	299.92	9.618	299.79	9.602	297.92	9.555	298.71	9.576
311.12	9.959	310.88	9.948	311.60	9.969	311.60	9.971	314.20	10.038
325.59	10.455	325.98	10.417	324.78	10.382	326.88	10.437	324.77	10.373
339.25	10.937	340.14	10.918	338.66	10.826	338.72	10.796	338.81	10.772
355.67	11.485	355.05	11.428	355.04	11.427	353.06	11.321	353.20	11.266
366.93	11.881	368.03	11.902	366.99	11.840	367.87	11.842	367.81	11.819
381.53	12.385	383.55	12.429	381.92	12.368	381.90	12.329	381.27	12.300
395.23	12.846	395.18	12.821	395.16	12.818	395.37	12.805	394.88	12.778
412.01	13.385	409.75	13.327	410.18	13.332	410.35	13.314	411.32	13.352
424.38	13.827	424.41	13.819	423.88	13.796	425.10	13.803	423.52	13.758
439.47	14.335	439.20	14.318	439.16	14.305	441.61	14.372	439.56	14.301
468.08	15.318	466.95	15.281	467.62	15.281	467.34	15.278	467.49	15.285
496.41	16.289	496.44	16.292	496.97	16.302	496.21	16.256	496.48	16.251
527.99	17.343	526.84	17.304	526.17	17.268	527.02	17.272	525.14	17.235
548.52	18.063		<i>a</i>	547.30	18.010	547.49	18.002	548.04	18.033
571.83	18.856			567.53	18.724	568.11	18.722	569.93	18.745
597.15	19.726			597.12	19.747	598.60	19.794	597.28	19.710
353.58	11.426	353.71	11.421	353.78	11.385	353.18	11.336	352.35	11.251

^a Values had to be left out due to decomposition. ^b An outlier had to be left out.

a vertical line in this figure. In principle, five points were available for the evaluation of the 598 K isotherm. One point was much too high due to any chemical alteration of the substance and has already been left out of the figure, whereas the remaining four are characterized by a comparably large scattering. Therefore, we decided to repeat the investigation of the viscosity of methanol vapor on the basis of a larger number of series of measurements, in particular at very low densities so that sufficient experimental points are available for the analysis of the initial density dependence of viscosity at low temperatures. In addition, due to a new experience derived from recent measurements on water vapor,⁵ we intended to determine the viscosity in the saturated vapor of methanol.

Experimental Section

The measurements were performed using an all-quartz oscillating-disk viscometer with small gaps. Details concerning the construction of the viscometer and its calibration, the implementation of the relative measurements, and their evaluation have been described in previous papers.^{6–8} The calibration of the apparatus according to the quasi-absolute theory of Newell⁹ requires only one calibration point at low densities. For that purpose, a reference value given by Kestin et al.¹⁰ for argon at room temperature was used. The performance of the viscometer was checked by determining the viscosity of argon at higher temperatures up to 600 K.

In general, the uncertainty is estimated to be $\pm 0.2\%$ at ambient temperature increasing up to $\pm 0.3\%$ at the highest temperature, whereas the reproducibility amounts to $\pm (0.1 \text{ and } 0.15)\%$, respectively. But the viscosity measurements on

methanol vapor could be influenced by any thermal alteration of the substance at high temperatures and at low densities. It is to be noted that some experimental points at low temperatures correspond to measurements in the saturated vapor.

Methanol was supplied by Riedel, de Haën, Germany, with a certified purity of $\geq 99.9\%$ and a maximum water content of 0.005%. In a special glass apparatus the substance was dried by molecular sieves 4A, degassed, and filled into small glass ampules. The purity of the samples in the ampules were checked by gas chromatography and mass spectrometry to be better than 99.9%. Ten series, each differing in density, were carried out at temperatures between (298 and 603) K and at densities from (0.004 to 0.050) $\text{mol}\cdot\text{dm}^{-3}$. The densities were obtained from the mass of the sample and the volume of the viscometer body.

To prove the occurrence of thermal decomposition, a check measurement was performed at a temperature near the boiling point after the highest temperature of the individual isochores had been attained. The results of these measurements show only a small increase in the viscosity coefficient compared with the first measurement at increasing temperature. But some values of three series of measurements were found to be much too high in comparison with those of the other isochores at higher temperatures and had to be left out. The reason for that is unclear, since Fisher et al.¹¹ did not observe significant thermal decomposition up to 630 K in a quartz-glass vessel. Our findings seem to demonstrate any reversible process, similar to those found in recent measurements on water vapor.⁵

The experimental results are summarized in Table 1. The values obtained for the check measurements are listed at the

end of each series of measurements. The experimental data of the isochores had to be recalculated into isothermal values by means of a first-order Taylor series, in terms of temperature:

$$\eta(T_{\text{int}}) = \eta(T_{\text{exp}}) + \left(\frac{\partial\eta}{\partial T}\right)_\rho \Delta T + R_N \quad (2)$$

$$\Delta T = T_{\text{int}} - T_{\text{exp}} \quad (3)$$

The interpolation temperature (T_{int}) is the average of the temperatures of the series of measurements considered for the further evaluation. The remainder (R_N) in eq 2 could be neglected in comparison with the experimental uncertainty. The temperature derivative of viscosity $(\partial\eta/\partial T)_\rho$ was derived using eq 4 with the respective coefficients that were deduced from a fit to the original isochoric data:

$$\eta(T) = S \exp\left(A \ln T_R + \frac{B}{T_R} + \frac{C}{T_R^2} + \frac{D}{T_R^3} + E\right)$$

$$T_R = \frac{T}{298.15 \text{ K}} \quad S = 10.0 \mu\text{Pa}\cdot\text{s} \quad (4)$$

Then, the analysis of the quasi-experimental isothermal values was carried out with a first-order expansion for the viscosity, in terms of density:

$$\eta(T, \rho) = \eta^{(0)}(T) + \eta^{(1)}(T)\rho \quad (5)$$

$$B_\eta(T) = \frac{\eta^{(1)}(T)}{\eta^{(0)}(T)} \quad (6)$$

The zero-density and initial-density viscosity coefficients ($\eta^{(0)}$ and $\eta^{(1)}$) were derived from the fit of eq 5. The second viscosity virial coefficient (B_η) followed from eq 6.

Furthermore, values for the viscosity of the saturated vapor were determined at low temperatures. For that purpose, the densities at saturation (ρ_s) were calculated using the equation of state¹. The viscosity coefficient corresponding to the saturated vapor (η_s) was obtained by averaging all viscosity values at densities higher than ρ_s . All results with their individual standard deviations (sd_{η_0} , sd_{η_1} , and sd_{η_s}) and with the standard deviations (sd_η) of each isotherm are listed in Table 2. With regard to a comparison with older experimental data from the literature, the results for the zero-density and initial-density viscosity coefficients according to eq 5 were used to derive viscosity coefficients at atmospheric pressure. The densities needed for the calculation were again deduced from the equation of state mentioned.

Figure 2 shows the initial density dependence of the viscosity at temperatures below the normal boiling point. The open circles represent the quasi-experimental values considered in the fit with eq 5, whereas the open triangles correspond to the points measured in the saturated vapor. Here it is to state that the densities in the figures cannot be identified with the densities at which the disk system was during the measurements. The viscosity coefficient at the true density at saturation was derived by averaging and is symbolized by a black triangle in each case. Figures 3 and 4 illustrate the initial density dependence for the isotherms at higher temperatures. Data points calculated at atmospheric pressure are shown as black circles. The viscosity values resulting from eq 5 are plotted as straight lines. Uncertainties of $\pm 0.1\%$ are indicated by error bars.

Theory

The zero-density viscosity coefficient ($\eta^{(0)}$) may reasonably be analyzed using the well-established kinetic theory of dilute

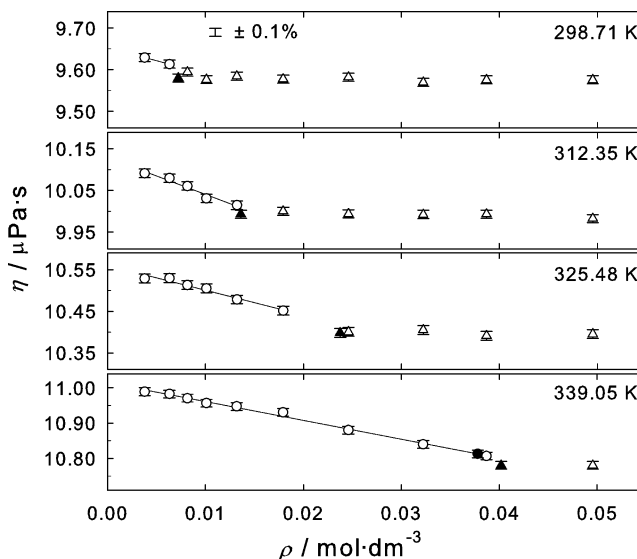


Figure 2. Viscosity of methanol vapor as a function of molar density for low isotherms. $\eta = \eta^{(0)} + \eta^{(1)}\rho$: \circ , quasi-experimental values; \triangle , values measured in the saturated vapor; \blacktriangle , value corresponding to the saturated vapor; \bullet , at 0.101325 MPa, calculated.

Table 2. Zero-Density and Initial-Density Viscosity Coefficients of Methanol Vapor for All Isotherms and Viscosity Coefficient of the Saturated Vapor

T K	$\eta_0 \pm \text{sd}_{\eta_0}$ $\mu\text{Pa}\cdot\text{s}$	$\eta_1 \pm \text{sd}_{\eta_1}$ $\mu\text{Pa}\cdot\text{s}\cdot\text{dm}^3\cdot\text{mol}^{-1}$	$\text{sd}_\eta \times 10^3$ $\mu\text{Pa}\cdot\text{s}$
298.71	9.653		
312.35	10.129 ± 0.009	-8.814 ± 1.000	7.18
325.48	10.560 ± 0.006	-5.937 ± 0.582	6.60
339.05	11.015 ± 0.003	-5.355 ± 0.160	5.51
353.92	11.501 ± 0.006	-4.026 ± 0.233	10.74
367.28	11.945 ± 0.003	-2.993 ± 0.107	4.94
381.68	12.429 ± 0.005	-2.426 ± 0.207	9.54
395.22	12.882 ± 0.005	-1.977 ± 0.180	8.30
410.60	13.412 ± 0.005	-1.986 ± 0.213	9.81
424.06	13.862 ± 0.006	-2.011 ± 0.241	11.13
439.35	14.381 ± 0.006	-2.047 ± 0.228	10.53
467.67	15.321 ± 0.005	-0.782 ± 0.181	7.43
496.51	16.298 ± 0.007	-0.741 ± 0.262	11.43
526.30	17.298 ± 0.007	-0.780 ± 0.264	11.02
547.44	18.023 ± 0.008	-0.349 ± 0.285	11.90
569.01	18.774 ± 0.017	-0.815 ± 0.574	22.05
598.18	19.778 ± 0.016	-0.413 ± 0.551	23.02

T K	ρ_s $\text{mol}\cdot\text{dm}^{-3}$	$\eta_s \pm \text{sd}_{\eta_s}$ $\mu\text{Pa}\cdot\text{s}$
298.71	0.007211	9.686 ± 0.003
312.35	0.013609	10.130 ± 0.003
325.48	0.023745	10.640 ± 0.003
339.05	0.040189	11.075^a

^a Only one value at saturation.

monatomic gases by Chapman and Enskog,¹² although in the case of a polyatomic molecule like methanol the influence of the intermolecular potential energy hypersurface and effects of higher-order terms for the coupling of the velocity and of the angular momentum of the molecules would have to be taken into consideration. Such a large-scale procedure has been applied only for linear molecules such as carbon dioxide^{13–15} until now. In this connection it is to point out that the calculation of the thermal conductivity requires additional measures due to the existence of internal degrees of freedom and to inelastic collisions.¹⁶

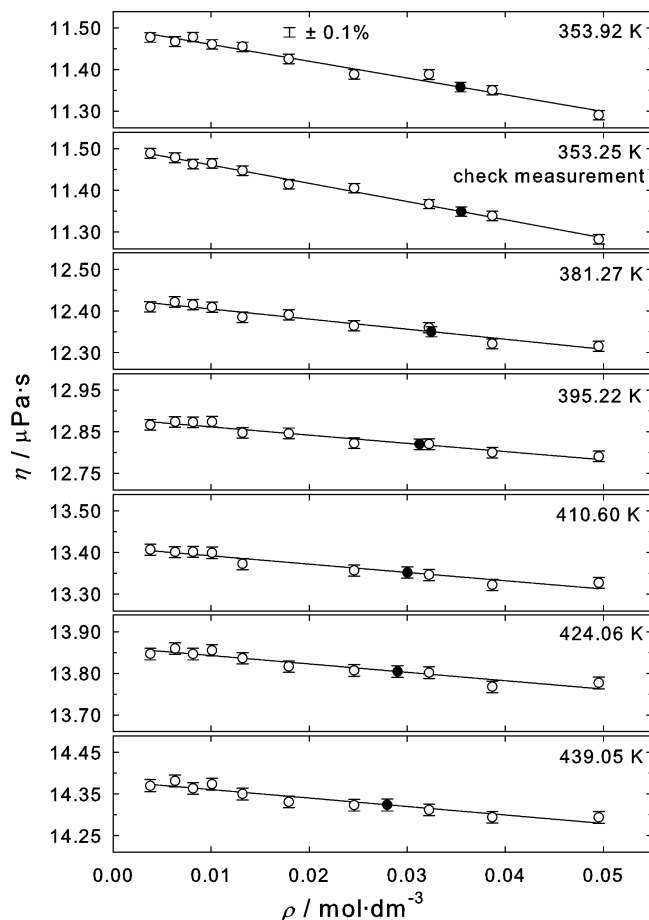


Figure 3. Viscosity of methanol vapor as a function of molar density for medium isotherms. $\eta = \eta^{(0)} + \eta^{(1)}\rho$: \circ , quasi-experimental values; \bullet , at 0.101325 MPa, calculated.

The analysis of $\eta^{(0)}$ in this paper is based on the theoretical relationship for the first-order approximation of the kinetic theory of dilute monatomic gases:¹⁷

$$\eta^{(0)}(T) = \frac{0.021357(MT)^{1/2}}{\sigma^2 S_{\eta}^*(T^*)} \quad (7)$$

$$T^* = k_B T / \epsilon \quad (8)$$

Here S_{η}^* represents a reduced effective cross section that contains all the dynamic and statistical information about the binary collisions including the effects of the different higher-order approximations. T^* is the reduced temperature, T is the temperature in K, whereas k_B is Boltzmann's constant. $\eta^{(0)}$ is given in units of $\mu\text{Pa}\cdot\text{s}$, when the length and energy scaling parameters (σ and ϵ/k_B) are in nm and K, and the molar mass (M) is in $\text{g}\cdot\text{mol}^{-1}$. With respect to the representation of experimental viscosity data by means of eq 7 without referring to an intermolecular potential hypersurface or to a simplified potential model, the temperature dependence of S_{η}^* may be described by the functional form:

$$\ln S_{\eta}^*(T^*) = \sum_{i=0}^4 a_i (\ln T^*)^i \quad (9)$$

Then the analysis and correlation of the zero-density viscosity coefficient using eqs 7 to 9 could be performed according to the extended corresponding states principle¹² strictly valid only for monatomic molecules such as rare gases. In a first step, a

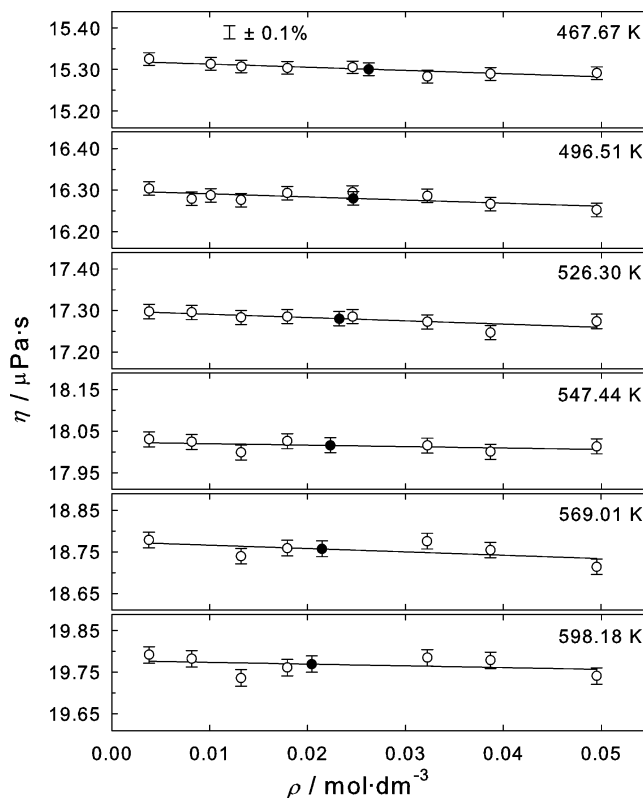


Figure 4. Viscosity of methanol vapor as a function of molar density for higher isotherms. $\eta = \eta^{(0)} + \eta^{(1)}\rho$: \circ , quasi-experimental values; \bullet , at 0.101325 MPa, calculated.

universal correlation was applied in the course of which the values of the scaling factors (σ and ϵ/k_B) for methanol were determined with use of the coefficients (a_i) of the functional S_{η}^* for the rare gases reported by Bich et al.¹⁸ It is obvious that such a universal correlation cannot represent appropriately the experimental viscosity data of a fluid like methanol. Then in an individual correlation, new values of the coefficients (a_i) were deduced by fitting eqs 7 to 9 again to the experimental viscosity values in the limit of zero density under the assumption that the scaling factors (σ and ϵ/k_B) remain the same as in the universal correlation.

The initial density dependence expressed as second viscosity virial coefficient (B_{η}) can be represented by means of the Rainwater–Friend theory.^{19,20} This theory models the second viscosity virial coefficient using the Lennard–Jones (12–6) potential for the interactions in the moderately dense gas. The theoretical expressions were fitted to selected experimental second transport virial coefficients including some for molecular gases, and tables of the reduced second viscosity virial coefficient (B_{η}^*) as a function of T^* were presented by Bich and Vogel.^{21,22} In addition, Vogel et al.²³ recommended an improved empirical expression for reduced temperatures between $0.5 \leq T^* \leq 100$, which can safely be extrapolated down to $T^* \approx 0.3$:

$$B_{\eta}^*(T^*) = \frac{B_{\eta}(T)}{NA\sigma^3} = \sum_{i=0}^6 b_i T^{*-0.25i} + b_7 T^{*-2.5} + b_8 T^{*-5.5} \quad (10)$$

Here B_{η} is in units $\text{dm}^3\cdot\text{mol}^{-1}$. N_A is Avogadro's constant. The coefficients b_i are listed by Vogel et al.²³ This empirical equation of B_{η}^* can be used to check the reliability of the experimental values of the second viscosity virial coefficient of methanol. Furthermore, experimental $\eta(T, \rho)$ data at a moderately low

Table 3. List of Available Data from Viscosity Measurements on Methanol Vapor at Low Densities

author(s)	T	p	no. of pts.	no. of iso. ^a	$\delta\eta_r^b$	method ^c	
	K	MPa			%		
Titani ²⁴	384–585	≈0.1	7	0	2.0	CAP	relative
Khalilov ²⁵	313–511	sat. vapor	22	0	5.0	CAP	absolute
Silgado and Storrow ²⁶	338–373	≈0.1	2	0	3.0	RB	relative
Craven and Lambert ²⁷	308–351	0.001–0.003	4	0	3.0	OSP	relative
Golubev and Petrov ^{28,29}	423–543	≈0.1	5	5	1.0	CAP	absolute
Golubev ³⁰	373–513	sat. vapor	17	0	1.0	CAP	absolute
Reid and Belenyessy ³¹	423	≈0.1	1	0	1.5	CAP	relative
Pal and Barua ³²	303–477	<0.01	5	0	3.0	OSD	relative
Golubev and Kovarskaya ³³	373–573	≈0.1	3	0	1.0	CAP	relative
Meerlender and Aziz ³⁴	343–353	≈0.1	2	0	1.0	CAP	relative
Golubev and Likhachev ³⁵	385–516	0.1–4.4 ^d	122	17	1.0	CAP	absolute
Vogel et al. ⁴	301–615	isochores	60	10	0.3	OSD	relative
Present paper	298–603	isochores	165	18	0.3	OSD	relative

^a Number of isotherms. ^b Ascribed relative uncertainty. ^c CAP, capillary; RB, rolling ball; OSP, oscillating pendulum; OSD, oscillating disk. ^d Maximum pressure of experimental points included in evaluation (see text).

density may be corrected to the limit of zero density using the following equation:

$$\eta^{(0)}(T) = \frac{\eta(T, \rho)}{1 + N_A \sigma^3 B_{\eta}^*(T^*) \rho} \quad (11)$$

Analysis Including Literature Data

Reliable data from the literature are needed in order to develop an appropriate viscosity surface correlation. Suitable data sets should be obtained from measurements with a high-precision instrument for which a full working equation is available and all necessary corrections can be applied. Our analysis, considering the viscosity of methanol vapor in the limit of zero density ($\eta^{(0)}$) and the second viscosity virial coefficient (B_{η}), requires experimental $\eta(T, \rho)$ values at moderately low densities.

An overview about the measurements available in the open literature in this density range including temperature range, pressures, number of points and isotherms, ascribed uncertainty, and measurement technique is given in Table 3. The oldest measurements on methanol vapor were carried out by Titani²⁴ in 1933, the most recent was by Vogel et al.⁴ in 1986. Four different measurement techniques are applied: relative and absolute capillary viscometers as well as rolling-ball, oscillating-pendulum, and oscillating-disk viscometers, all in a relative manner. For the comparison with the present values, the temperatures of all earlier data were converted to the ITS-90 temperature scale.

First, the data from the literature were grouped into data sets at about atmospheric pressure (Titani,²⁴ Silgado and Storrow,²⁶ Golubev and Petrov,^{28,29} Reid and Belenyessy,³¹ Golubev and Kovarskaya,³³ Meerlender and Aziz³⁴) and data sets near or extrapolated to zero density (Craven and Lambert,²⁷ Pal and Barua,³² Golubev and Likhachev,³⁵ Vogel et al.⁴). In this connection, it is to note that the measurements by Golubev and Likhachev³⁵ were performed up to higher pressures starting with atmospheric pressure. We have evaluated their data with a first-order expansion for the viscosity, in terms of density, to derive the zero-density and the initial-density viscosity coefficients. The results are summarized in Table 4. The density range of these data that corresponds to an expansion, linear in density, is much larger than that of our measurements. Hence, the values of the standard deviation (sd_{η_1}) of the initial-density viscosity coefficient are smaller than for our results, whereas the values of the standard deviation (sd_{η}) for the complete isotherm are smaller in the case of our measurements. On the other hand, all

Table 4. Zero-Density and Initial-Density Viscosity Coefficients of Methanol Vapor Derived from the Isothermal Experimental Data of Golubev and Likhachev³⁵

T	$\eta_0 \pm sd_{\eta_0}$	$\eta_1 \pm sd_{\eta_1}$	$sd_{\eta} \times 10^3$	
K	$\mu\text{Pa}\cdot\text{s}$	$\mu\text{Pa}\cdot\text{s}\cdot\text{dm}^3\cdot\text{mol}^{-1}$	$\mu\text{Pa}\cdot\text{s}$	no. of pts ^a
384.82	12.646 ± 0.002	−5.009 ± 0.024	1.12	3 (3)
385.12	12.664 ± 0.008	−4.865 ± 0.114	5.31	3 (3)
396.12	12.978 ± 0.020	−3.347 ± 0.184	17.09	3 (3)
396.72	13.004 ± 0.021	−3.205 ± 0.189	17.58	3 (3)
405.12	13.312 ± 0.020	−2.915 ± 0.119	20.61	5 (5)
405.62	13.342 ± 0.011	−2.920 ± 0.075	11.10	4 (4)
417.32	13.649 ± 0.015	−2.281 ± 0.073	18.77	6 (6)
422.52	13.907 ± 0.014	−2.097 ± 0.063	19.17	10 (10)
440.11	14.477 ± 0.011	−1.511 ± 0.033	18.69	9 (13)
445.31	14.637 ± 0.024	−1.266 ± 0.068	42.45	9 (13)
463.41	15.265 ± 0.017	−0.853 ± 0.033	29.05	10 (18)
483.21	15.933 ± 0.011	−0.463 ± 0.017	21.95	12 (20)
503.21	16.606 ± 0.014	−0.247 ± 0.016	22.32	9 (22)
509.71	16.800 ± 0.011	−0.083 ± 0.024	22.25	9 (29)
513.11	16.929 ± 0.010	0.065 ± 0.016	16.73	8 (25)
514.51	17.016 ± 0.007	0.103 ± 0.012	13.71	10 (32)
515.71	17.070 ± 0.012	0.183 ± 0.022	20.27	9 (24)

^a Number of isothermal points included in evaluation. Numbers in parentheses correspond to points of complete isotherm.

of the data by Golubev and Likhachev could not be included in the evaluation with eq 5, they would require an expansion with higher terms in density. The number of isothermal points included in the evaluation is given in the last column of Table 4. The highest pressure of a measuring point considered in the evaluation is given in Table 3 for the data of Golubev and Likhachev.

The viscosity data from the literature are compared with calculated values of the present paper at atmospheric pressure in Figure 5. The analogous comparison in the limit of zero density is shown in Figure 6 in which the data of Pal and Barua³² are excluded since they are characterized by unexplainable large deviations of about −(5 to 7) %. In principle, a sufficient number of measurements were performed at low densities (near to atmospheric pressure), but most of them do not fulfill the demands on primary reliable data sets. Figure 5 shows that the data of Titani,²⁴ Silgado and Storrow,²⁶ Golubev and Petrov,^{28,29} and Golubev and Kovarskaya³³ deviate systematically from the values of the present paper. Such differences, particularly at lower temperatures, are not acceptable for primary data sets used for the development of a viscosity surface correlation. One reason for these positive deviations could be that measurements on organic vapors such as methanol have often been influenced by incomplete degassing of the substance resulting in increased viscosity values due to air inside the sample. Furthermore, data

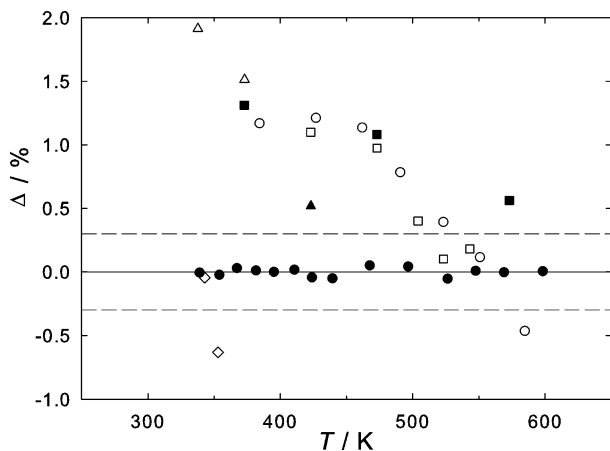


Figure 5. Deviations $\Delta = 100(\eta_{lit} - \eta_{exp,fit})/\eta_{exp,fit}$ of viscosity data of the literature from the present results obtained by a fit of eq 4 to the calculated values at atmospheric pressure: \circ , Titani;²⁴ \triangle , Silgado and Storrow;²⁶ \square , Golubev and Petrov;^{28,29} \blacktriangle , Reid and Belenyessy;³¹ \blacksquare , Golubev and Kovarskaya;³³ \diamond , Meerlender and Aziz;³⁴ \bullet , present paper.

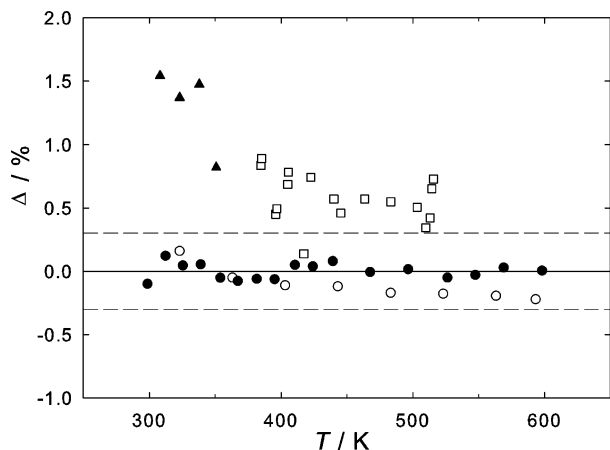


Figure 6. Deviations $\Delta = 100(\eta_{lit} - \eta_{exp,fit})/\eta_{exp,fit}$ of viscosity data of the literature from the present results obtained by a fit of eq 4 to the values in the limit of zero density: \blacktriangle , Craven and Lambert;²⁷ \square , Golubev and Likhachev;³⁵ \circ , Vogel et al.;⁴ \bullet , present paper.

sets consisting of one or two points (Reid and Belenyessy³¹ as well as Meerlender and Aziz³⁴) cannot substantially support the determination of the correlation although these values agree well with those of the present paper. On the other hand, the comparison for the limit of zero density in Figure 6 makes evident that in a reasonably large temperature range the data of Golubev and Likhachev,³⁵ of Vogel et al.,⁴ and of the present paper agree within $\pm 1\%$, the last two data sets even within $\pm 0.3\%$. Therefore, these three data sets should be used for the zero-density viscosity correlation.

As already discussed in the foregoing section, the correlation of the zero-density viscosity coefficient was performed in two steps. Experimental S_η ($S_\eta = \pi\sigma^2 S_\eta^*$) values were deduced from the selected primary data via eq 7 using appropriate statistical weights w_k following from

$$w_k = \left(\frac{100}{\eta_{exp,k} \delta\eta_{r,k}} \right)^2 \quad (12)$$

Here, $\eta_{exp,k}$ and $\delta\eta_{r,k}$ are the k th experimental viscosity value and its relative uncertainty as given in Table 3. $\delta\eta_r$ was ascribed on the basis of the measurement method, the quoted experimental error, the check on precision of the data, and the discrepancies in overlapping thermodynamic ranges for measurements on further gases or vapors.

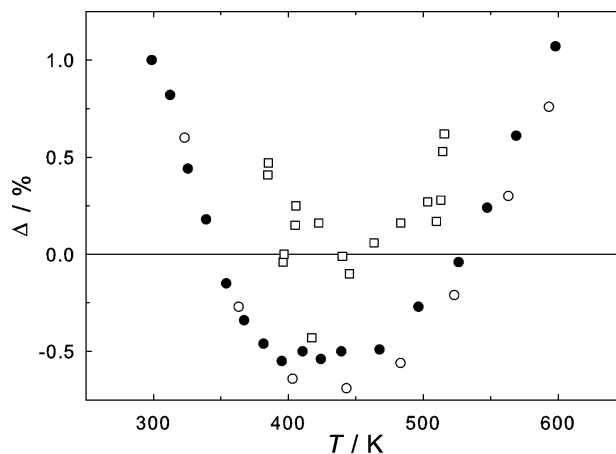


Figure 7. Deviations $\Delta = 100(\eta_{exp} - \eta_{cor})/\eta_{exp}$ of viscosity data from the universal zero-density viscosity correlation: \square , Golubev and Likhachev;³⁵ \circ , Vogel et al.;⁴ \bullet , present paper.

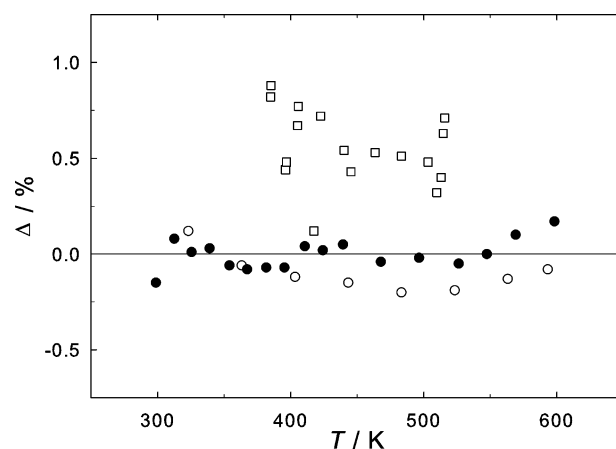


Figure 8. Deviations $\Delta = 100(\eta_{exp} - \eta_{cor})/\eta_{exp}$ of viscosity data from the present individual zero-density viscosity correlation: \square , Golubev and Likhachev;³⁵ \circ , Vogel et al.;⁴ \bullet , present paper.

The following scaling factors were obtained for methanol vapor as the result of the universal correlation:

$$\sigma = 0.36994 \text{ nm} \quad \epsilon/k_B = 462.00 \text{ K}$$

The differences between the correlated values and the experimental data are plotted in Figure 7, which reveals that the universal correlation cannot adequately describe the viscosity coefficient in the limit of zero density. In the second step an individual correlation was performed in which new coefficients a_i of the functional $S_\eta^*(T^*)$ were determined:

$$a_0 = 0.22663022 \quad a_1 = -0.52859173 \\ a_2 = -0.0011434132 \quad a_3 = 0.0 \quad a_4 = 0.0$$

These individual coefficients are valid for the temperature range (298 to 598) K. The deviations of the experimentally based data from the individual correlation are shown in Figure 8. The figure makes clear that the present correlation is suitable to represent the experimental data within their uncertainties.

The results of B_η obtained from $\eta^{(1)}$ and $\eta^{(0)}$ via eq 6 for the data of Golubev and Likhachev,³⁵ of Vogel et al.,⁴ and of the present paper are used to correlate the second viscosity virial coefficient. In the fitting process of eq 10 to the experimentally based B_η values (all with the same statistical weight), the following scaling factors σ and ϵ/k_B were derived:

$$\sigma = 0.62740 \text{ nm} \quad \epsilon/k_B = 418.11 \text{ K}$$

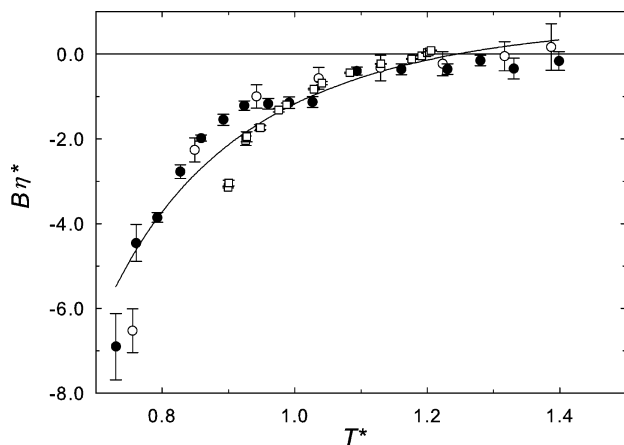


Figure 9. Reduced second viscosity virial coefficient (B_{η}^*) as a function of the reduced temperature (T^*). \square , Golubev and Likhachev;³⁵ \circ , Vogel et al.;⁴ \bullet , present paper; —, Rainwater–Friend theory, Vogel et al.²³

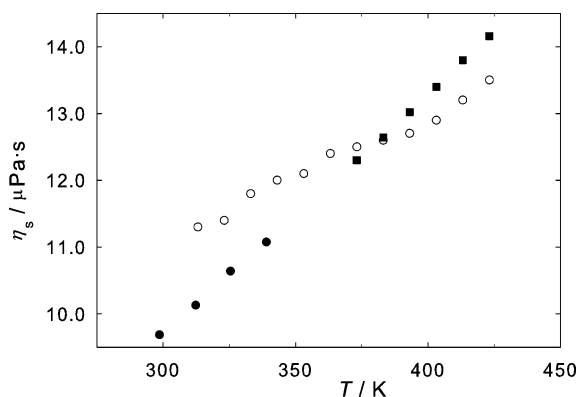


Figure 10. Comparison of data for the viscosity coefficient of the saturated vapor (η_s): \circ , Khalilov;²⁵ \blacksquare , Golubev;³⁰ \bullet , present paper.

The curve of the Rainwater–Friend theory for the reduced second viscosity virial coefficient and the reduced experimental B_{η}^* values are illustrated in Figure 9. Uncertainties derived from the standard deviations sd_{η_1} are indicated by error bars. Here it is to note that the error bars for the B_{η}^* values of Golubev and Likhachev³⁵ are within the size of the symbol due to the small values of sd_{η_1} . The figure demonstrates that the experimental B_{η} values are appropriately described by the Rainwater–Friend theory.

In addition, our results for the viscosity of the saturated vapor could be compared with the data of Khalilov²⁵ as well as Golubev³⁰ as shown in Figure 10. The data of Khalilov are approximately 10 % higher than our values in the overlapping temperature range and are characterized by a very peculiar temperature dependence, if the data of Golubev are additionally considered. Finally, the comparison of the present values with the data of Golubev demonstrates that both data sets are mutually consistent.

Conclusions

The results of new viscosity measurements in the density range from (0.004 to 0.050) mol·dm⁻³ at temperatures between (298 and 603) K agree with those of older measurements performed in our laboratory at nearly the same temperatures and densities within ± 0.3 %. The inspection of viscosity data from the literature at moderately low densities makes clear that most of them do not fulfill the requirements on primary data sets. The comparison of the viscosity values of the present paper with the data by Golubev and Likhachev³⁵ shows mutual

agreement within ± 1 % in the comparably large temperature range from (385 to 516) K. Although the values of the present paper and the data of Golubev³⁰ for the saturated vapor were not determined at the same temperatures, it is obvious that they are characterized by a reasonable good consistency. Taking into account that the measurements of Golubev and Likhachev³⁵ were extended up to higher pressures in the vapor phase below the critical temperature, we propose to use their values together with the data of Golubev,³⁰ of Vogel et al.,⁴ and of the present paper for the development of the viscosity surface correlation in the complete vapor phase region below the critical temperature and in the low-density range up to 615 K.

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