Registry No. 1,1,2,2-tetrachloroethane, 79-34-5; methyl ethyl ketone, 78-93-3; diethyl ketone, 96-22-0; methyl propyl ketone, 107-87-9.

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Viscosity of Liquid-Phase Methyl Chloride

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A high-pressure capillary viscosimeter was used to measure the viscosity of liquid-phase methyl chloride in the temperature range from 20 to 150 °C. The constants of the apparatus were evaluated by calibration with gases of known viscosity. The precision of the measurements is estimated to be ±1% in the normal liquid range and ±5% in the critical region.

Introduction

Several sets of measurements of the viscosity of liquid-phase methyl chloride have been reported in the literature (*1–4*). With the exception of the very old data of ref *4*, results are not reported for temperatures above 50 °C. In addition, there are wide discrepancies among the several sets of data, amounting to nearly a 50% spread at temperatures in the range from 20 to 50 °C.

This paper describes the construction and calibration of a high-pressure capillary viscometer and its subsequent use to measure the viscosity of liquid-phase methyl chloride in the temperature range from 20 to 150 °C. The instrument was designed as a device of moderate precision suitable for gathering data of satisfactory accuracy for engineering purposes. It was not intended to be a primary device. The constants of the apparatus were evaluted by calibration with reference fluids of known viscosity. Parameters of the apparatus were chosen so as to minimize the capillary inlet correction.

Description of the Method

The apparatus (Figure 1) is a steady-flow capillary device similar in concept to the devices used by Flynn, Hanks, Lemaire, and Ross (*5*), by Kao, Ruska, and Kobayashi (*6*), and by Sun and Storvick (*7*). The capillary is a 141.78-mm length of fused silica chromatographic tubing with a nominal inside diameter of 200 μm supported inside a section of 3.2 mm o.d., 0.5 mm i.d. stainless steel tubing. Flow through the capillary is established by the coupled movement of two identical piston injectors driven by a synchronous motor through an adjustable gear train.

The pressure differential across the capillary is measured by a Sensotec wet/wet differential pressure transducer with a full-scale range of ±0.5 psid and nominal accuracy of ±0.5%. Total pressure is measured with a 2000 psig Heise Bourdon tube gauge accurate to ±1 psig.

Water jackets on the piston injectors maintain the temperature at 25 ∓ 0.1 °C, and the temperature of the capillary is established by a water or oil bath (depending on the temperature) within a tolerance of ±0.01 °C.

The modified Poiseuille equation for the viscosity in terms of the experimental parameters is

$$\eta = \eta_p - mX \tag{1}$$

where

$$\eta_p = \pi a^4 \Delta p / (8 Q L_{\text{eff}}) \tag{2}$$

$$X = \rho Q / (8 \pi L_{\text{eff}}) \tag{3}$$

and where a = capillary radius, Δp = pressure difference across the capillary, Q = volumetric flow rate, m = inlet correction factor, L_{eff} = effective length of capillary, and ρ = density of fluid. The slip correction, the Couette correction, and the thermal expansion of the capillary are negligible for the conditions of the experiments reported here.

According to Kestin, Sokolov, and Wakeham (*8*), the inlet correction factor m is a function of the Reynolds number. The relationship between m and the Reynolds number was evaluated from numerical calculations based on an assumed flow model for a capillary viscometer. According to ref *8*, the results of the calculations are represented with adequate accuracy in the range $2 < \text{Re} < 200$ by

$$m = m_0 + 16n/\text{Re} \tag{4}$$

where

$$m_0 = 1.17 \pm 0.03$$

$$n = 0.69 \pm 0.004$$

and where Re is the Reynolds number based on the capillary diameter. The above relationship can be used for a Reynolds numbers greater than 200 provided that laminar flow is preserved.

A second result of the work reported in ref *8* is that the effective length of the capillary is given by

$$L_{\text{eff}} = L + na$$

The result, however, is not pertinent to this investigation be-

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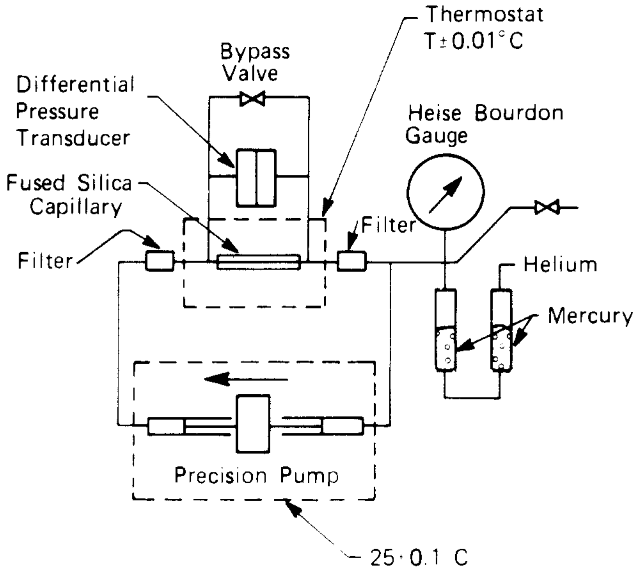

Figure 1. Experimental viscometer.

Table I. Calibration of Experimental Viscometer with Helium at 25 °C and 0.444 MPa

flow rate, mL/h	Δp, kPa	X, μPa·s	η(ref *9*), μPa·s	$10^{16}a^4/L_{\mathrm{eff}}$, m^3
120.51	2.216	0.007	19.853	7.577
48.20	0.888	0.003		7.561
24.10	0.444	0.001		7.560
				av 7.566 ± 0.008

cause the adjustment to the length is compensated for in the calibration procedure.

Calibration

The apparatus was calibrated with compressed helium gas at 25 °C by using a reference value from Kestin, Ro, and Wakeham (*9*). Viscometer data at 0.444 MPa were used to establish the value of the constant

$$C = a^4/L_{\mathrm{eff}}$$

with the results given in Table I. The average value of the constant is equivalent to an effective diameter of 203.54 μm, which is in quite good agreement with the nominal value given by the manufacturer of the tubing.

The response of the differential pressure transducer is somewhat influenced by the total pressure in the system. In lieu of an explicit calibration of the instrument, a pressure correction factor correlation was developed from measurements with helium at 25 °C in the pressure range from 1.11 to 10.44 MPa again using the values of Kestin, Ro, and Wakeham as reference. The maximum correction was found to be 2.4% at the maximum working pressure of the system, 10.44 MPa.

Viscosity of Compressed Nitrogen

As a check on system response, the viscosity of nitrogen at 25 °C was determined in the pressure range from 0.444 to 6.99 MPa. The results are given in Table II along with values interpolated from Kestin and Leidenfrost (*10*). The differences relative to the Kestin and Leidenfrost data are substantially smaller than one would expect on the basis of the precision of these measurements, which is estimated to be ±1%.

Viscosity of Methyl Chloride

Experimental data were gathered for methyl chloride at 3.55, 6.99, and 10.44 MPa and at temperatures of 20, 40, 60, 90, 120, and 150 °C. Significant pressure fluctuations were observed during the liquid-phase displacements. In order to get satisfactory precision, a laboratory computer was used to record and average the pressure measurements during the displacement process. In a typical run a standard deviation of ±1% was obtained for approximately 150 readings of the pressure differential.

Table II. Verification of Viscometer Performances with Compressed Nitrogen at 25 °C

p, MPa	Q, mL/h	Re	X, μPa·s	η, μPa·s	η (ref *10*), μPa·s	difference, %
0.444	120.51	59	0.47	17.851	17.843	+0.04
	48.20	24	0.19	17.904		+0.34
	24.10	12	0.09	17.853		+0.06
1.134	120.51	150	1.21	17.947	17.934	+0.07
	48.20	60	0.48	17.916		−0.10
	24.10	30	0.24	17.944		+0.06
2.168	120.51	284	2.31	18.131	18.096	+0.19
	48.20	114	0.92	18.078		−0.10
	24.10	57	0.46	18.194		+0.54
4.243	120.51	545	4.52	18.478	18.479	−0.01
	48.20	218	1.81	28.489		−0.16
	24.10	109	0.01	18.462		−0.09
6.994	120.51	866	7.44	19.135	19.164	−0.15
	48.20	346	2.98	19.050		−0.60
	24.10	173	1.49	18.990		−0.92

Table III. Viscosity of Methyl Chloride

t, °C	p, MPa	Q_0,[a] mL/h	Re	10^3X, Pa·s	$10^3\eta$, Pa·s
20	3.555	12.051	103	0.0009	0.1858
	3.5666	6.026	52	0.0004	0.1854
40	3.557	12.051	123	0.0009	0.1560
		6.026	62	0.0004	0.1553
60	3.546	24.10	297	0.0017	0.1295
		12.051	149	0.0009	0.1290
90	3.546	24.10	393	0.0017	0.0981
		12.051	196	0.0009	0.0979
	6.991	24.10	367	0.0017	0.1048
		12.051	183	0.0009	0.1051
120	6.991	24.10	510	0.0017	0.0756
		12.051	254	0.0009	0.0757
	10.44	24.10	457	0.0017	0.0842
		12.051	231	0.0009	0.0835
150	6.992	24.10	1848	0.0017	0.0228
		12.051	924	0.0009	0.0219
					0.0210[b]
	10.44	24.10	671	0.0017	0.0597
		12.051	335	0.0009	0.0584
		12.051	335	0.0009	0.0588
					0.0574[b]

[a] Flow rate at 25 °C pump temperature. [b] Extrapolated to $Q_0 = 0$.

Results of the measurements are given in Table III and in Figure 2. Density values required for reduction of the data were taken from Hsu and McKetta (*11*) and from the Matheson Gas Data Book (*12*).

The pressure differential at each experimental point was measured at two flow rates. Intermediate rates could not be set because the minimum step in the adjustment of the pump transmission was a factor of 2. At flow rates lower than those reported the precision of the pressure measurement was unsatisfactory, and at higher flow rates the range of the differential pressure cell was exceeded.

With the exception of one point in the critical region, the maximum capillary inlet correction amounted to approximately 3.4% of the corrected viscosity. Most values were much smaller. The experimental Reynolds numbers, with the same exception, were within the range 50–1000.

Corrected results for the two flow rates did not differ significantly except at 150 °C in the critical region. The corrected

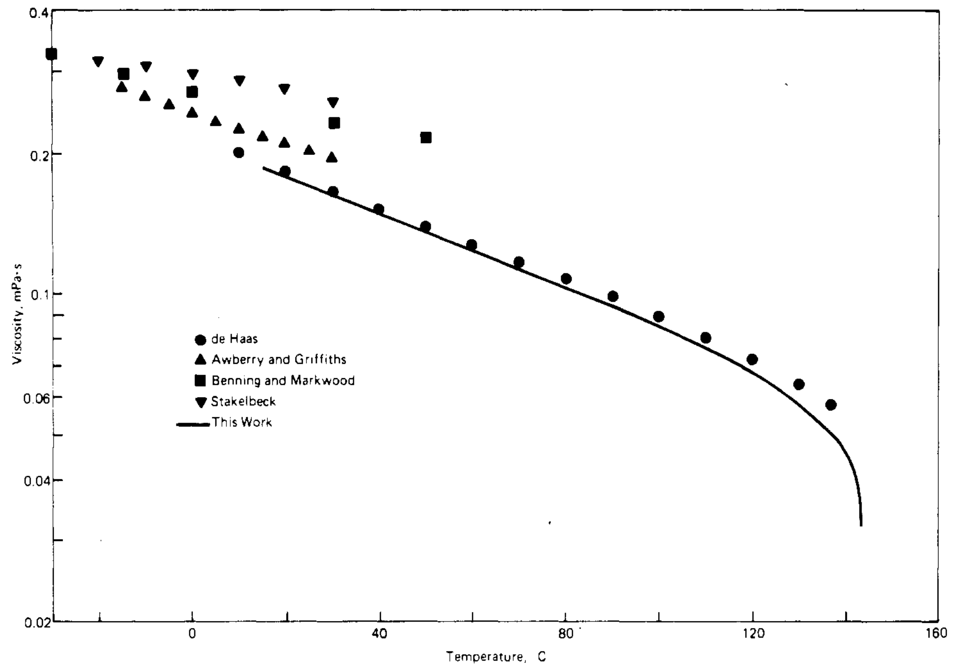

Figure 2. Viscosity of saturated liquid-phase methyl chloride.

Table IV. Viscosity of Saturated Methyl Chloride

t, °C	$10^3\eta$, Pa·s	t, °C	$10^3\eta$, Pa·s
20	0.1788	120	0.067 76
40	0.1484	130	0.058 43
60	0.1237	140	0.046 09
80	0.1035	143.1	0.031 97
100	0.08473		

apparent viscosities at 6.99 and 10.44 MPa at this temperature show a significant trend toward lower values at lower flow rates. The trend suggests that temperature equilibration at the capillary entrance was incomplete. Accordingly, the two sets of data were extrapolated to zero flow and the extrapolated values are also given in Table III. It should be noted, however, that as the result of proximity to critical conditions (143.1 °C and 6.68 MPa) differential pressure fluctuations were rather severe during the measurements; thus, the experimental uncertainty at 6.99 MPa and 150 °C is estimated to be ±5% and that at 10.44 MPa and 150 °C, ±3%.

The viscosity at saturation conditions is given in Table IV. These values were estimated by using an equation of the form suggested by Dymond and Brawn (*13*) on the basis of smooth hard-sphere theory:

$$\ln \eta' = A + B'/(V - V_0) \qquad (5)$$

where

$$\eta' = \eta V^{2/3}/(MT)^{1/2} \qquad (6)$$

and where V is the molar volume, V_0 is the molar volume of close packing, M is the molecular weight, and A and B' are empirically determined constants. V_0 is normally slightly temperature dependent; however, the data of this investigation were not extensive enough to evaluate the temperature dependence; thus, V_0 was considered to be constant at an average value.

The quantities A, B' and V_0 were selected by simplex optimization to give the best fit to the data with the following result in SI units: $A = -18.0643$, $B' = 27.614 \times 10^{-6}$ m^3, $V_0 = 37.038 \times 10^{-6}$ m^3. The standard deviation for the fit was 2.1%. (The equivalent value of A is $-0.794\,93$ in the units used in ref *13*.)

Figure 2 is a plot of viscosity at saturation conditions as a function of temperature for the results of this investigation and for the data available in the literature. The current measurements agree reasonably well with the very old data of de Haas (*4*) but fall substantially below the results of Stakelbeck (*3*) and Benning and Markwood (*2*) and somewhat below those of Awbery and Griffiths (*1*).

Materials

Helium and prepurified nitrogen were used as received. Methyl chloride purchased from the Matheson Co. was degassed by vacuum pumping at 77 K, and water was removed by passing the vapor at room temperature over 4A molecular sieve. A mass-spectrometric scan from mass 12 to mass 100 revealed no peaks which could be ascribed to impurities (sensitivity: 0.3%).

Registry No. Methyl chloride, 74-87-3.

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