Measurements of the Thermal Conductivity and Viscosity of Liquid Propylene

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We have measured the thermal conductivity and viscosity of liquid propylene near room temperature. Thermal conductivity measurements were made from 5 to 56 °C and from saturated vapor pressure to about 90 bar by using a hot-wire technique; viscosity measurements were made from 10 to 60 °C and from slightly above saturated vapor pressure to about 40 bar by using a capillary viscometer calibrated with distilled water. We estimate the overall uncertainties to be ±3% for the thermal conductivity data and ±1.5% for the viscosity data.

Introduction

Propylene (C_3H_6) is an attractive fluid for use in liquid-working-substance heat engines (*1*) because its critical temperature of 91.7 °C is near room temperature and because its Prandtl number is low. In order to understand operation of heat engines using liquid propylene, accurate thermal conductivity and viscosity data are required. We undertook the measurements described in this paper because existing data (*2–5*) on the transport properties of propylene near room temperature are scarce and are inconsistent with each other.

The samples used for both the thermal conductivity and viscosity measurements were polymer-grade propylene (Scientific Gas Products, South Plainfield, NJ); the supplier claims the impurities are less than 1% propane, 20 ppm oxygen, and 5 ppm water. The samples were distilled into the measuring apparatus directly from the shipping container.

Viscosity

The simple capillary viscometer used for the viscosity measurements is shown in Figure 1. The flow impedance consists of a 17-cm-long CuNi capillary with 0.013-cm inside diameter and 0.010-cm wall. The two standpipes are ordinary glass 1-mL pipets about 30 cm long with 0.25-cm inside diameter. These components are mounted on two support plates, separated by threaded rods. All metal-to-metal joints are sealed with soft solder, and the glass-to-metal joints are sealed with fluorocarbon rubber O rings. The tops of the pipets are connected through valves to sources of propylene and high-pressure nitrogen. The entire viscometer, including the valves, is immersed in temperature-controlled water inside a transparent acrylic container.

The viscometer is filled with liquid to a level such that the pipets are about half full, and pressurized with nitrogen if desired. The two valves and the nitrogen pressure are manipulated to establish a difference between the liquid levels in the two pipets. A measurement of viscosity is then made by opening both valves and recording the height h of the liquid in one pipet as a function of time t. This is accomplished by watching the liquid level and manually triggering a microcomputer to read its internal clock each time the liquid level passes one of the 0.01-mL graduations on the pipet. After the liquid level difference has dropped to about 10% of its initial value, the computer fits the function

$$h(t) = h_0 + h_1 e^{-t/\tau} \qquad (1)$$

to the data by the method of least squares, with h_0, h_1, and the time constant τ all adjustable. A typical set of data displaying the excellent fit to eq 1 is shown in Figure 2. The time constant is extracted with a precision of about 1% and is independent of average liquid level, which pipet is observed for the measurements, and whether the observations are made on the rising liquid level or the falling liquid level.

The kinematic viscosity $\nu = \eta/\rho_L$ is related to τ by

$$\nu = (2g\tau/ZA)(1 - \rho_G/\rho_L) \qquad (2)$$

where η is the dynamic viscosity, g is the acceleration of gravity, Z is the viscous flow impedance factor of the capillary, A is the cross-sectional area of the standpipes, and ρ_L and ρ_G are the liquid and gas densities. The factor $2g/ZA$ is obtained by calibrating the apparatus with distilled water at 20 °C, by using the accepted value (*6*) $\nu = 0.01004$ cm^2/s for the viscosity of water. The densities ρ_L and ρ_G are obtained from ref *7* and *8*, with the assumptions that in the gas the partial pressure of propylene is its saturated vapor pressure and the partial pressure of nitrogen equals the total pressure minus the propylene partial pressure; we estimate that deviations from this behavior caused by increased chemical potential in the liquid (*9*) and by nonideality in the gas mixture (*10*) are less than 0.3%. Errors arising from kinetic energy effects at the capillary ends and from incomplete drainage of liquid in the pipet above the falling liquid level are estimated (*11*) to be less than 0.3%.

To be sure that the flow impedance of the capillary did not change (because of foreign particles, for example) during this work, we took the data in the following order: (1) Measurements were made with propylene at 20 °C, yielding the results shown as open squares in Figure 3. (2) A calibration run was performed with distilled water at 20 °C, yielding a time constant of 953 s. (3) The rest of the propylene measurements were performed and are displayed as open circles in Figure 3; at 20 °C the agreement with the earlier measurements was excellent. (4) Two more calibrations with distilled water at 20 °C were performed, yielding time constants of 960 and 953 s, in agreement with the first calibration. The curve through the data is the equation

$$\eta = 2.7503 - 12.954\rho + 17.997\rho^2 \qquad (3)$$

with ρ in g/cm^3 and η in millipoise. Also plotted are two sets of published results (*2*, *3*) at saturated vapor pressure, in poor agreement with our results and with each other. Our data are fully tabulated in Table I. We estimate the overall uncertainty in the measurements to be ±1.5%.

Thermal Conductivity

The hot-wire technique for the measurement of thermal conductivity has been described extensively elsewhere (*12*, *13*). In this work we used the technique to measure the conductivity of propylene, checking our apparatus by measuring the well-documented conductivity of toluene. The measurement is based on the relationship between the temperature change of a wire, upon sudden application of uniform heating, to the thermal conductivity of the fluid surrounding the wire. For

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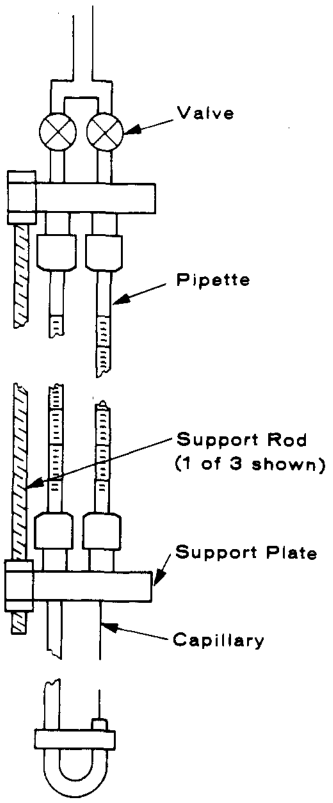

Figure 1. Sketch of the viscometer, not to scale.

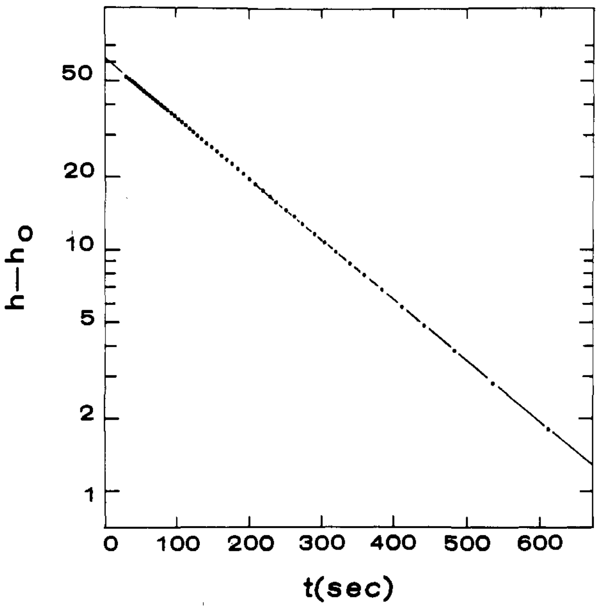

Figure 2. Typical height vs. time data for propylene showing the good fit to eq 1. The height h is measured in units of the 0.01-mL graduations of the pipets, about 0.2 cm.

relatively large diameter wires (0.025 mm) in propylene, the temperature change of the wire after initial (<50 ms) transients have decayed is (*14*)

$$\Delta T(t) = \frac{q}{4\pi\lambda}\ln\frac{4\kappa t}{a^2 C} + \frac{a^2}{2\kappa t} + \frac{a^2}{2t}\left(\frac{1}{\kappa} - \frac{\rho_w C_w}{\lambda}\right)\ln\frac{4\kappa t}{a^2 C} \qquad (4)$$

where q is the power dissipated per unit length in the wire, λ is the thermal conductivity of the fluid, a is the wire radius, κ is the thermal diffusivity of the fluid, ρ_w is the density of the wire, C_w is the specific heat of the wire, C is 1.781..., and t is time. For platinum, ρ_w = 21.45 g/cm^3, C_w = 0.0317 cal/(g °C) (*15*).

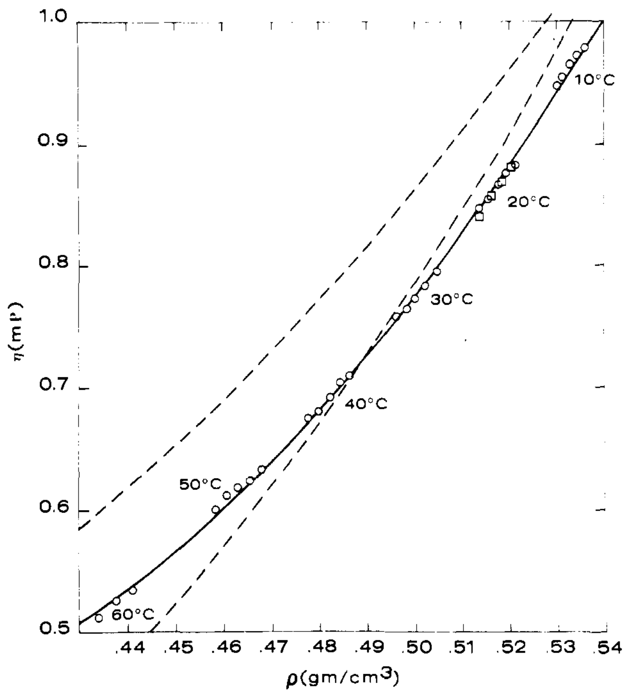

Figure 3. Dynamic viscosity of propylene vs. density for six different temperatures. The open symbols are the results of this work, and the solid line is eq 3. The upper and lower dashed lines are from ref *3* and *2*, respectively.

Table I. Kinematic Viscosity of Propylene

P, bar	$10^3\nu$, cm^2/s	P, bar	$10^3\nu$, cm^2/s
	T = 10 °C		
11.03	1.782	26.27	1.817
14.82	1.791	32.40	1.821
20.55	1.807		
	T = 20 °C		
13.17	1.649	28.89	1.675
13.93	1.635	31.92	1.686
18.89	1.658	35.09	1.696
20.82	1.662	38.20	1.697
25.85	1.675		
	T = 30 °C		
16.00	1.529	32.13	1.560
21.37	1.535	39.23	1.575
26.13	1.545		
	T = 40 °C		
19.17	1.410	33.51	1.452
23.44	1.415	38.54	1.459
28.27	1.432		
	T = 50 °C		
25.10	1.306	36.96	1.339
28.61	1.322	41.23	1.351
32.47	1.332		
	T = 60 °C		
27.58	1.178	36.06	1.208
31.78	1.197		

Our hot-wire thermal conductivity apparatus is similar to that of Roder (*13*). The case holding the wires was made from commercially pure titanium because the thermal expansion coefficients of platinum, used for the wires, and titanium are nearly the same at the temperatures of interest, thereby eliminating problems associated with changes in wire tension from differential thermal expansion. The two wires (Hudson Wire, Ossining, NY) were 0.002 54-cm diameter platinum. We chose this diameter for ease of handling and reproducibility of wire properties. The wires were stripped of insulation by soaking in concentrated H_2SO_4 for 15 min and then in 30% H_2O_2 for

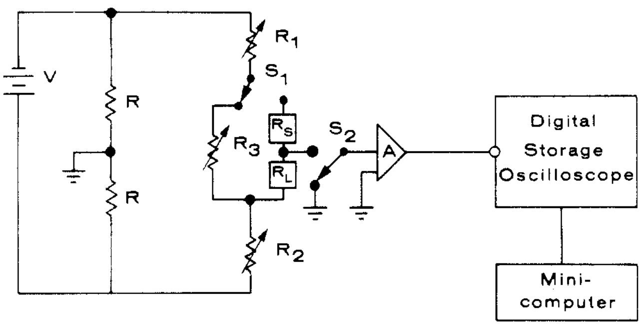

Figure 4. Circuit used for measurement of thermal conductivity.

1 h and then rinsing in distilled water. The wires were tensioned by soldering one end into the upper feedthrough, threading the other end through the lower feedthrough, and then soldering a 2.5-g weight to the free end. With the apparatus vertical, the tensioned wire was then soldered to the second feedthrough and the weight cut off. The wires were not annealed after installation. The case and wire assembly were contained in an aluminum pressure vessel immersed in a temperature-controlled water bath, regulated to be constant to within ±0.005 °C. The pressure vessel had leveling screws so that the wires could be aligned vertically to within ±0.05%.

Because the wires act as both heat source and thermometer, their temperature coefficient of resistance must be measured. The effects of possible strain or nonuniformity require that each wire be calibrated separately. This was done in a constant-temperature bath of toluene at temperatues from 5 to 50 °C. We took care to ensure that power applied to the wires during calibration was low enough to prevent detectable heating. We found that over the temperature range of interest the wires fit linear equations accurately enough that no T^2 corrections were necessary; the resistance of the long wire is $R_L = 28.19\ \Omega + (0.1077\ \Omega/°C)T$ and the resistance of the short wire is $R_S = 11.95\ \Omega + (0.0456\ \Omega/°C)T$ with T in °C. Maximum deviation of the data from these fits was ±0.005 Ω for the long wire and ±0.003 Ω for the short wire. We estimate the local slope errors to be less than ±0.5%. The copper leads (No. 16 solid wire) which connected the bridge to the cell had a small but measurable resistance, as did the power supply leads. These together introduced corrections of 0.6%. The ratio of wire lengths (17.512 cm/7.338 cm = 2.3865) agreed with the ratio of resistances at 0 °C (2.3590) and with the ratios of dR/dT (2.3593), indicating that the calibration was internally consistent and the wires were probably homogeneous.

The circuit used for all thermal conductivity measurements is shown in Figure 4. The voltage supply consisted of a lead–acid storage battery, which provided power to a semiconductor voltage regulator and filter capacitor (to improve transient response). This supply provided from 4.7 to 5.0 V to the bridge during our measurements. Switches S1 and S2 were fast mercury-wetted relays, which were energized simultaneously to initiate a measurement. Switch S1 enabled us to maintain constant the current drawn from the supply and the current through R_1 and R_2 before and after the wires were heated. This was accomplished by setting $R_3 = R_L + R_S$. Setting $R_1 = R_L$ and $R_2 = R_S$ ensured that the power per unit length dissipated in the wires was, to first order, independent of R_S or R_L. Resistors R were 100.00-Ω ultraprecision wire-wound resistors. We designed amplifier A to have less than 2 μV/°C drift, a gain of 10, and a gain flat to 1 part in 10^6 to 30 kHz. Switch S2 was closed just as the wire began to heat to prevent the amplifier from overloading before the measurement began. The amplifier was connected to a 12-bit by 12-bit digital storage oscilloscope. Digitized data were read into and processed by a minicomputer. To ensure that we knew when power was first applied to the wire, one channel of the oscilloscope was connected to a buffer amplifier which detected voltage across the wires. This signal was analyzed by the minicomputer to determine $t = 0$ to within 500 μs. Actual data were taken for 1 s after the wires began to heat at 500-μs intervals, and eq 4 was fitted to the data obtained between 50 ms and 1 s. To determine the stability of the entire electronics assembly, fixed stable resistors were inserted in place of the platinum wires; a measurement was then made as if to determine the thermal conductivity. We found that the resulting data record was constant in time to within the amplifier noise, a satisfactory result.

The procedure used for obtaining each thermal conductivity datum was as follows. We began by setting the pressure and adjusting the controller to regulate the bath at the desired temperature. Before a measurement was taken, we waited 1 h while holding the bath temperature constant. Actual temperature was measured with a mercury-in-glass thermometer which could be read to ±0.01 °C. During the wait for equilibrium, we set resistors R_1, R_2, and R_3 to the appropriate values. The bridge excitation supply remained on. Once we were certain of equilibrium, we measured the bath temperature, the bridge excitation voltage, and, with a laboratory Bourdon-tube gauge, the fluid pressure. The conductivity measurement was then started by activating S1 and S2, and a wave form was recorded and stored in the computer. Immediately after storage was completed, we calibrated the sensitivity of the bridge. This was accomplished by changing the decade resistor R_2 by 0.1 Ω and recording the step change in the bridge output voltage on the digital oscilloscope. This measured gain always agreed within ±0.3% with the gain calculated from knowledge of the supply voltage and resistances in the arms of the bridge.

In order to fit our data to eq 4, we needed a value of κ, which we obtained from the specific heat and density data of ref *7* for propylene and from ref *4* for toluene. The fit is extremely insensitive to the values of these parameters; a 10% error in specific heat or density causes a 0.3% error in conductivity. In addition, during the course of a measurement, the temperature of the wire changed by approximately 4 °C. This effect was also corrected for (*12*).

To check the overall accuracy of our apparatus, we measured the thermal conductivity of toluene. Because toluene has thermal properties roughly similar to propylene, a test with it should be indicative of the performance with propylene. Furthermore, extensive measurements have been made by others (*16*–*19*) of the thermal conductivity of toluene in the temperature range of interest. For this test we used two grades of toluene (Reagent and Nanograde, Mallinckrodt, St. Louis, MO) and found no difference in thermal conductivity. Our data for toluene agree with some previously published results (*16*) but are higher than most (*17*–*19*); the total spread of literature values is about 3% and our results fall within 0.3% of the higher ones.

The reproducibility of our toluene data was about ±0.2%. Various tests were performed to check the sensitivity of the measurement to external parameters; no detectable change in measured conductivity was observed for tilts from verticality of 0.25%, changes in bridge excitation by a factor of 2, changes in toluene pressure by a factor of 2, or increases in ambient magnetic field by a factor of 50.

Our data for propylene are shown in tabular form in Table II and in graphical form in Figure 5. The data fitted the equation

$$K = 1.614 + (1.91 \times 10^{-3})T - 6.709\rho + 10.771\rho^2 \quad (5)$$

with K in mW/(cm K), T in °C, and ρ in g/cm^3. Equation 5 is plotted in Figure 5 as a set of solid lines, one for each of the seven temperatures T at which data were taken, and another line for $T = T_{SVP}(\rho)$ the saturated vapor pressure curve. The results of ref *5* at saturated vapor pressure are also shown. In

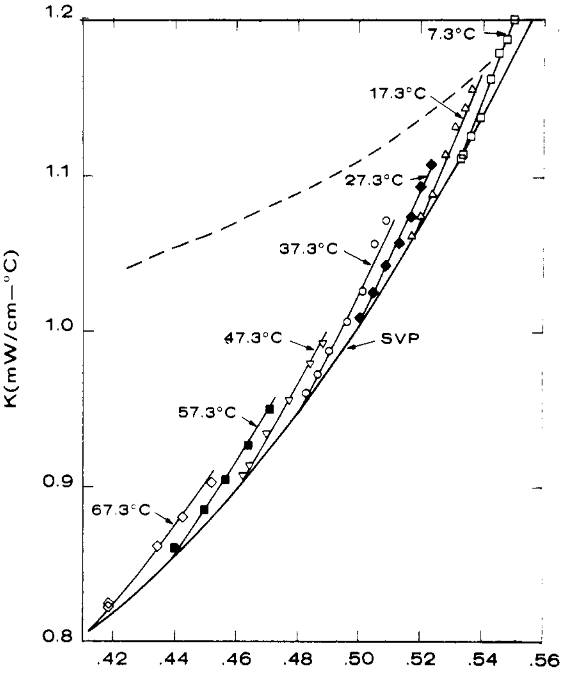

Figure 5. Thermal conductivity of propylene. The solid lines represent eq 5 and the dashed line the results of ref *5* at saturated vapor pressure.

Table II. Thermal Conductivity of Propylene

T, °C	P, bar	λ, mW/(cm °C)	T, °C	P, bar	λ, mW/(cm °C)
7.32	8.00	1.105	37.41	17.65	0.954
7.35	11.51	1.107	37.37	26.41	0.966
7.34	11.58	1.108	37.39	35.92	0.982
7.30	20.96	1.120	37.33	51.92	1.001
7.28	34.06	1.131	37.30	66.53	1.020
7.25	49.50	1.156	37.28	79.36	1.051
7.23	62.12	1.172	37.25	92.04	1.066
7.23	76.32	1.181	47.31	20.20	0.901
7.11	86.67	1.193	47.30	23.99	0.908
17.43	10.96	1.056	47.27	34.13	0.928
17.41	20.68	1.069	47.22	49.64	0.950
17.38	34.47	1.082	47.18	65.84	0.974
17.31	50.19	1.108	47.22	76.19	0.986
17.28	64.26	1.126	57.16	24.61	0.855
17.24	77.63	1.138	57.26	37.99	0.880
17.23	87.97	1.150	57.23	49.02	0.899
27.28	13.31	1.003	57.21	62.53	0.921
27.27	24.96	1.019	57.02	76.60	0.944
27.34	38.40	1.037	67.34	34.47	0.818
27.31	52.40	1.051	67.34	34.47	0.817
27.24	66.26	1.068	67.35	51.30	0.855
27.21	77.98	1.087	67.28	62.88	0.874
27.20	92.11	1.101	67.19	77.63	0.898

Figure 6, we show a typical data set as taken from our digitizer and the least-squares fit to eq 4. As a check of the reproducibility, the data at 7 °C include both the first (8.0–34.1 bar) and last (49.5–86.7 bar) measurements made during the 5 days required to obtain the data; no mismatch between the low- and high-pressure data at 7 °C can be detected. Our results fall below those of ref *2*, *4*, and *5*.

We estimate the overall uncertainty in these results to arise from the following sources. The uncertainty in $d(R_L - R_S)/dT$ is ±1%. Nonlinearities in the bridge contribute ±0.1%, while uncertainty in bridge gain is ±0.3%, and in bridge excitation voltage ±0.05%. The uncertainty in temperature measurement introduces an error of not more than ±0.1% directly and ±0.03% because of the resulting error in knowing the wire resistance. Errors in the specific heat data (*7*) may be as high as 10%, introducing uncertainty in our data of ±0.3%. Finally, radiation corrections (*12*) might amount to ±0.8%. Assuming these uncertainties to be uncorrelated gives an overall uncertainty of ±1.4%, while the worst-case error is ±2.4%. We note that our data for toluene are 3% higher than the lowest values (*19*) found in the literature. Therefore, we conservatively estimate the overall uncertainty in our results to be ±3%.

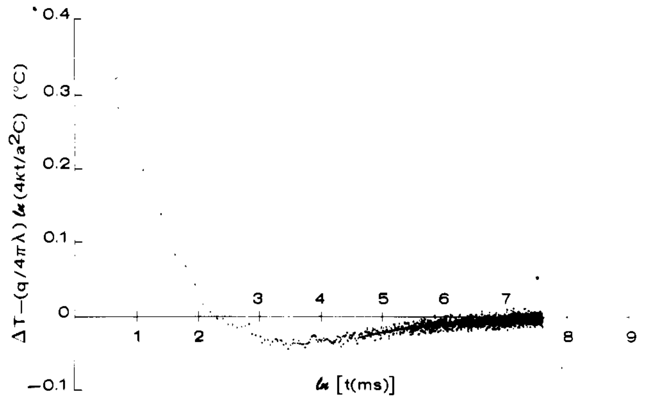

Figure 6. Typical data set for a thermal conductivity measurement of propylene, as plotted by our minicomputer. The solid line is the fit to eq 4. The quantity $(q/4\pi\lambda)\ \ln\ (4\kappa t/a^2C)$ has been subtracted from each data point and from the fit to emphasize deviations from logarithmic behavior.

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Registry No. Propylene, 115-07-1.

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