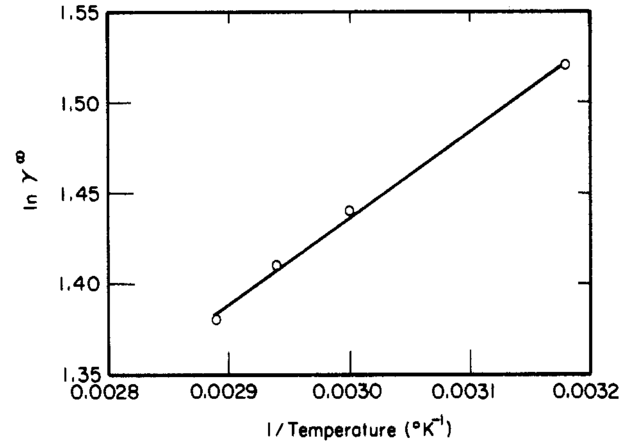

Figure 4. Limiting activity coefficient data for 2-nitropropane in carbon tetrachloride.

Acknowledgment

We thank W. S. Templin, Union Carbide Corp., and J. Gall and T. Schmidt of Phillips Petroleum Co. for their excellent suggestions concerning the ebulliometer design. We also thank C. Henderson, D. Husa, P. Burban, and J. Ankenbauer for their help in measuring the data.

Glossary

γ^∞	limiting activity coefficient
$\bar{h}_i^E$	partial molar excess enthalpy
ϕ	vapor-phase fugacity coefficient
ϕ^s	fugacity coefficient at saturation pressure
P	total pressure
P^s	saturation pressure
R	gas constant
V	liquid molar volume
x	liquid-phase mole fraction

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Measurements of the Viscosity of Saturated and Compressed Liquid Propane

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The shear viscosity coefficient of saturated and compressed liquid propane has been measured with a torsionally oscillating quartz crystal viscometer at temperatures between 90 and 300 K and at pressures up to 30 MPa (4350 psia). The estimated precision and accuracy of the measurements are about 1% and 2%, respectively. The measurements have been compared with an equation previously optimized to available data and proposed for calculating the viscosity of compressed gaseous and liquid propane at temperatures down to 140 K. Differences between the equation and the measurements reported here are within our experimental error at temperatures above 140 K. Differences between our measurements and the equation extrapolated to temperatures below 140 K increase with decreasing temperature (and increasing density) to about 30% at 90 K.

Introduction

This research is part of a long-range program on the thermophysical properties of compressed and liquefied hydrocarbon gases and their mixtures. The purpose of this report is to provide accurate wide-range viscosity measurements at low temperatures and liquid densities for testing and improving an equation previously proposed (*1*) for calculating the dependence of the shear viscosity coefficient of compressed gaseous and liquid propane on temperature and density.

The technical importance of propane is well-known: propane is an important constituent in both liquefied natural gas (LNG) and liquefield petroleum gases (LPG). Propane has an unusually long vapor pressure-reduced temperature curve, extending down to a reduced temperature of about 0.23 at low temperatures. Therefore, the thermophysical properties of propane are useful as the reference state in corresponding states calculations of the properties of higher molecular weight hydrocarbon fluids and their mixtures.

This report provides new absolute viscosity measurements for saturated and compressed liquid propane at temperatures between 90 and 300 K and at pressures to 30 MPa (4350 psia). The measurements have been compared with an equation previously proposed (*1*) for calculating the viscosity of propane at temperatures down to 140 K. The differences between the equation and the measurements reported here are discussed in detail.

Experimental Section

The measurement method, apparatus, and procedures are essentially the same as reported in our work on other fluids (*2*,

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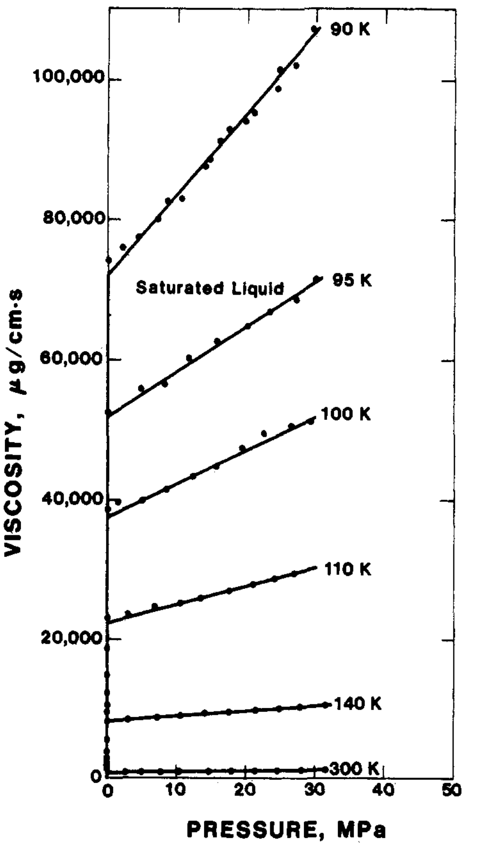

Figure 1. Viscosity of compressed liquid propane as a function of pressure.

3). Only details specific to this work are reported here.

The same torsionally oscillating quartz crystal of approximately 5-cm length and 0.5-cm diameter, discussed in ref *2*, was used for these measurements. The measurements were performed on commercial research-grade propane, used without further purification. The minimum purity of the propane was claimed to be 99.98%, with the most likely impurity being ethane.

Densities were obtained from measured temperatures and pressures and an equation of state reported by Goodwin (*4*) to represent the wide-range $P-V-T$ properties of propane. The estimated error of the calculated densities is believed to be less than 0.2%.

Viscosities were derived from the measured crystal resonance-curve bandwidths, Δf, using the equation

$$\eta = \frac{\pi f}{\rho}\left[\frac{M}{S}\right]^2\left[\frac{\Delta f}{f} - \frac{\Delta f_{vac}}{f_{vac}}\right]^2 \qquad (1)$$

where ρ is the fluid density, and M, S, and f are the mass, the surface area, and the resonant frequency of the crystal, respectively. This equation, based on an analysis of the instrument by Webeler (*5*), has been used to derive all of the viscosities reported by this laboratory.

The bandwidth of the resonance curve under vacuum, Δf_{vac}, was measured with an imprecision of about 5% and ranged from 0.020 Hz at 90 K to about 0.090 Hz at 300 K.

The initial pressures (about 30 MPa) for the isothermal measurements were obtained by compressing a liquid sample from the supply cylinder with a commercially available, diaphragm-type compressor.

Results and Discussion

Measurements of the viscosity of compressed liquid propane are presented in Table I and in Figures 1 and 2. Measurements were made as a function of pressure and density along six isotherms at temperatures between 90 and 300 K and at pressures to about 30 MPa (4350 psia). The estimated precision of our measurements in this range is about 1%, somewhat larger than that obtained when the viscosity-density product is 1 order of magnitude smaller. This is due mainly to the very broad, flat conductance-frequency behavior obtained for fluids having large viscosity-density products. In this temperature and pressure range the viscosity of liquid propane increases linearly with pressure at fixed temperature. The viscosities obtained at the lowest temperatures and highest densities are substantially larger than any that we have measured previously. The dependence of the viscosity on density and temperature is similar to that of other fluids that we have examined (*2*, *3*). Although the temperature dependence at fixed density is quite weak, the viscosity of the compressed liquid is clearly smaller than that of the saturated liquid at the same density and at a lower temperature.

Table I. Viscosity of Compressed Liquid Propane along Isotherms

P,[a] MPa	ρ,[b] mol/L	η,[c] µg/(cm s)	P,[a] MPa	ρ,[b] mol/L	η,[c] µg/(cm s)
$T = 300.00$ K					
31.4819	12.4158	1 424.8	14.4867	11.8357	1 185.4
27.9618	12.3128	1 395.2	10.3143	11.6484	1 119.5
24.5522	12.2059	1 354.0	8.0612	11.5353	1 080.1
21.5115	12.1037	1 294.0	5.0105	11.3647	1 029.4
17.9339	11.9734	1 243.2	2.5213	11.2058	986.9
$T = 140.00$ K					
31.4887	15.6941	10 829.4	14.1296	15.5278	9 396.0
27.9307	15.6617	10 541.3	10.5874	15.4911	8 907.3
24.5968	15.6306	9 990.2	7.2345	15.4554	8 750.5
21.2840	15.5989	9 968.0	2.9560	15.4084	8 500.2
17.6018	15.5628	9 787.1			
$T = 110.00$ K					
27.0587	16.2765	29 298.1	13.4966	16.1741	25 933.3
24.3793	16.2570	28 753.2	10.4841	16.1501	15 074.2
21.1592	16.2330	27 858.3	7.0079	16.1218	24 483.8
17.6491	16.2064	26 899.8	3.0584	16.0887	23 510.4
$T = 100.00$ K					
29.3194	16.4997	50 819.4	12.1309	16.3816	43 208.7
26.5155	16.4813	50 369.1	8.4628	16.3548	41 391.5
22.5620	16.4547	49 360.6	4.9997	16.3288	39 941.8
19.2760	16.4322	47 112.2	1.7048	16.3035	39 443.8
15.5088	16.4058	44 741.9			
$T = 95.00$ K					
30.1526	16.6085	71 354.5	11.7928	16.4884	59 923.6
27.1553	16.5898	68 477.0	8.2591	16.4638	56 153.1
23.6359	16.5674	66 927.9	4.9662	16.4403	55 595.9
20.1914	16.5450	64 774.8	1.9640	16.4184	52 925.4
15.7148	16.5152	62 473.4			
$T = 90.00$ K					
29.5052	16.7081	107 221.0	14.7578	16.6170	88 727.8
27.4100	16.6957	102 151.1	14.1280	16.6129	87 649.2
24.8692	16.6803	101 215.4	10.8870	16.5917	82 927.7
24.5790	16.6786	98 669.1	8.8250	16.5780	82 636.3
21.3692	16.6588	95 220.4	7.2960	16.5677	79 791.8
20.0883	16.6508	93 977.5	4.7275	16.5583	77 410.2
17.7389	16.6361	92 741.1	2.4083	16.5342	75 797.3
16.3425	16.8272	91 311.5			

[a] Pressure. [b] Density. [c] Viscosity.

The measurements were compared with an equation previously proposed (*1*) for calculating the viscosity of propane at temperatures between 140 and 500 K and at pressures to 50 MPa. This equation was used to correlate all previous data for the viscosity of propane in this temperature and pressure range. Figure 3 shows comparisons between our measurements and the equation for the 300 K isotherm. The differences are less than our estimated experimental error (2%) throughout the entire pressure and density range. The differences between our measurements and the correlation increase somewhat with

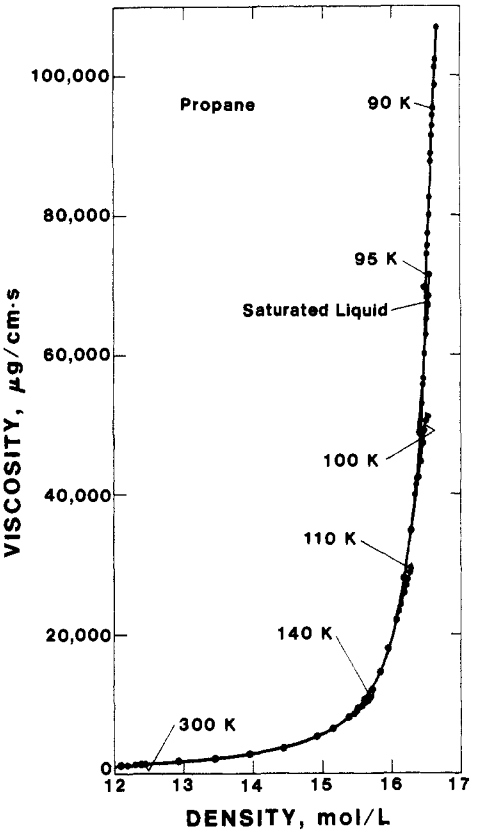

Figure 2. Viscosity of saturated and compressed liquid propane as a function of density.

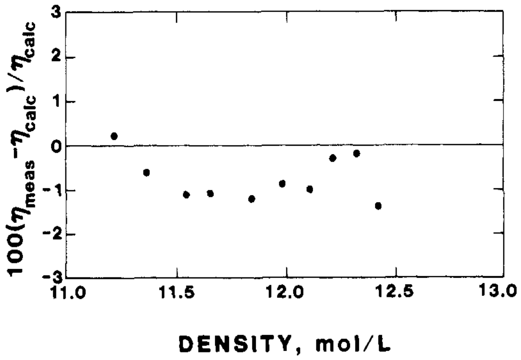

Figure 3. Comparison of measured and calculated (*1*) viscosities for compressed liquid propane at 300 K and pressures to 30 MPa. The horizontal line represents calculated viscosities (*1*).

Table II. Viscosity of Saturated Liquid Propane

T,^{a} K	ρ,^{b} mol/L	η,^{c} μg/(cm s)	T,^{a} K	ρ,^{b} mol/L	η,^{c} μg/(cm s)
90.00	16.517	74172.5	160.00	14.910	5458.6
95.00	16.404	52109.0	170.00	14.676	4528.2
100.00	16.290	38195.2	180.00	14.438	3816.3
105.00	16.177	28638.1	190.00	14.198	3355.4
110.00	16.063	22866.4	200.00	13.954	2867.5
115.00	15.949	18449.8	220.00	13.454	2243.2
120.00	15.834	15263.5	240.00	12.930	1798.7
125.00	15.720	12676.6	260.00	12.373	1437.8
130.00	15.605	10846.1	270.00	12.078	1297.6
135.00	15.490	9555.6	280.00	11.769	1171.2
140.00	15.375	8321.7	290.00	11.442	1050.4
150.00	15.144	6590.6	300.00	11.095	959.4

[a] Temperature. [b] Densities from ref *4*. [c] Viscosity.

decreasing temperature, reaching a maximum of about 6% at 140 K and 30 MPa.

Measurements of the viscosity of saturated liquid propane at temperatures between 90 and 300 K are presented in Table II.

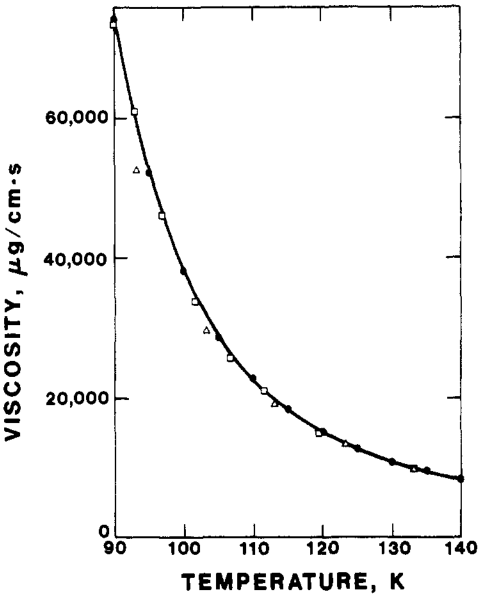

Figure 4. Viscosity of saturated liquid propane as a function of temperature between 90 and 140 K: (●) our measurements; (□) Gerf and Galkov (*6*); (△) Swift, Christy, and Kurata (*7*).

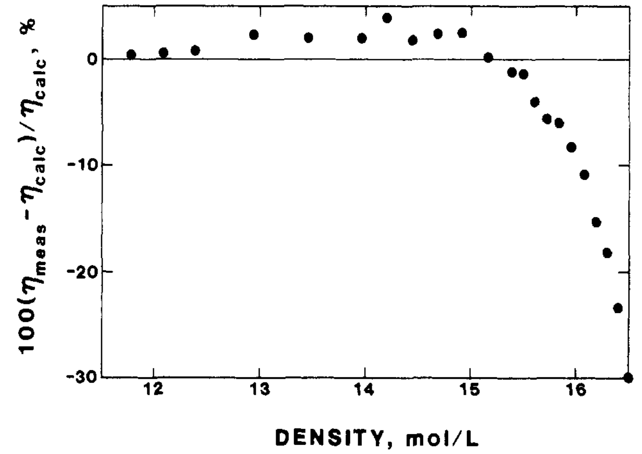

Figure 5. Comparison of measured and calculated (*1*) viscosities for saturated liquid propane, 90–300 K. The horizontal line represents calculated viscosities (*1*).

Figure 4 shows a comparison between previous capillary tube measurements (*6*), falling cylinder measurements (*7*), and our measurements in the temperature range 90–140 K. The capillary tube measurements agree with our measurements within our experimental error. The differences between the falling cylinder measurements and our measurements are somewhat larger, reaching a maximum difference of about 12% at the lowest temperature. The differences between our measurements on saturated liquid propane and the proposed equation are shown in Figure 5. At temperatures above 140 K (and densities less than 15.4 mol/L) most of the differences are within our experimental error. At temperatures below 140 K, however, the differences between our measurements and the extrapolated equation increase with decreasing temperature and increasing density to a maximum of about 30% at 90 K. Our measurements extend previous low-temperature measurements to higher pressures and densities and can be used to improve correlations and predictive models in this density range.

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Solubility of Carbon Dioxide in Propylene Carbonate at Elevated Pressures and Higher than Ambient Temperatures

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Solubility data of carbon dioxide in propylene carbonate at pressures ranging from 13.6 to 68 atm (200–1000 psia) and at temperatures from 26.7 to 104.4 °C (80–220 °F) are presented. The Krichevsky–Kasarnovsky solubility equation, which has been known to work well with a very dilute system, also predicted solubility well at substantial finite concentrations, in excellent agreement with the experimental data to an average accuracy of 1.09% with a maximum deviation of 2.7%. The Henry's law constants obtained from the current data through extremely low pressure extrapolation showed good agreement with literature values and were used in the prediction of solubility of carbon dioxide. Values of the constants are 81.7 atm at 80 °F, 103.5 atm at 100 °F, 159.4 atm at 160 °F, and 227.8 atm at 220 °F. An attempt has been made to predict the solubility of carbon dioxide in propylene carbonate by using the Krichevsky–Ilinskaya (K–I) equation, which contains a liquid-phase activity coefficient. However, the equation did not improve the predictions.

Introduction

Application of propylene carbonate at elevated pressures and at higher than ambient temperatures as a carbon dioxide absorbing agent is common practice in the sweetening process of natural gas. The absorbing agent may perform a rather important role in the treatment of carbon dioxide rich gas for the enhanced oil recovery process. However, the solubility data for carbon dioxide in propylene carbonate at possible design conditions are very limited.

This study was conducted to determine the solubility of gaseous carbon dioxide in propylene carbonate at 80 °F and of supercritical carbon dioxide in the same solvent at temperatures of 100, 160, and 220 °F and to provide a correlation of the data.

Experimental Section

Apparatus. The experimental equipment, consisting of an equilibrium cell, a pressure maintenance arrangement, and an analytical train, is, in principle, the same as the design described by Kobayashi (*3*). Figure 1 shows a schematic diagram of the experimental apparatus.

The equilibrium apparatus consisting of a high-pressure windowed cell rated to hold pressures up to 10 000 psia was mounted in a constant-temperature air bath. The gas charge line was connected to the top of the cell, and the liquid sampling line was drawn from the bottom of the cell. Constant temperature was maintained within ±0.1 °F in the bath by electrical heating coils installed in the circulated air. The temperature of the cell was measured by a thermocouple connected to a Leeds and Northrup precision portable potentiometer. Cell pressure was measured by a calibrated 2000-psi Heise gauge with 2-psi subdivisions.

A gas cylinder, a gas reservoir, and a mercury displacement pump were used for the pressure maintenance scheme, and also to charge the cell with gas at pressures greater than that in the gas cylinder.

The analytical train consists of a buret used as a flash chamber for the liquid phase, a drying tube to remove foreign matter from the flash gas, a manometer to measure the sample pressure, and a flask of predetermined volume into which the flash gas expanded. A three-way stopcock at the top of the flask was used to evacuate the system. The tubing connections were made with India rubber tubing impregnated with paraffin wax.

Reagents. Carbon dioxide of a purity of 99.6 mol % was purchased from the Spencer Chemical Co. The propylene carbonate was obtained from the Jefferson Chemical Co. with a minimum purity of 99 wt %. The densities of the carbon dioxide and the propylene carbonate at 25 °C and 1 atm were 0.001 808 and 1.190 g/cm^3, respectively, as given in ref *4* and *5*.

Procedure. The cell was charged initially with propylene carbonate. The cell was agitated while it was charged with carbon dioxide. After a period when there was no further pressure drop with time, the cylinder valve was closed and the system further agitated for at least 1 h at constant temperature. The system was allowed to sit for at least 2 h at the same constant temperature before sampling.

The sampling tube was flushed with about 5 cm^3 of the equilibrium liquid in the cell into a beaker. Then, the tube was connected to the analytical train. The analytical train was evacuated and allowed to sit for 5 min to check for any leak. The valve on the sampling tube was opened to allow liquid sample to pass into the buret. When about 10 cm^3 of flush liquid was collected in the buret, the valve was closed. The

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