Viscosities and Densities of Methane-Propane Mixtures at Low Temperatures and High Pressures

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The viscosities and densities of methane-propane mixtures were determined at pressures to 5,000 lb./sq.in.abs. for 22.1 and 50.0 mole % methane over a temperature range from —120 to 37.78°C. and for 75.3 mole % methane over a temperature range from —150° to 37.78°C. Reproducibility of the viscosity data was ± 2%, and the agreement with literature values was, on the average, within ± 2%. The reproducibility of the density data was ± 0.8%, and the agreement with literature values was ± 1.2% .

Viscosity data for mixtures of light paraffin hydrocarbons at low temperatures are almost nonexistent. Lim et al. (*10*) measured liquid viscosities of methane-propane, methane–*n*-butane, and ethane–*n*-butane mixtures. Those data were not well correlated by available methods (*4*, 9), thereby raising some questions on their reliability. An experimental program was initiated as a result to provide thorough and consistent data coverage on one of these systems, the methane-propane system, since it was recognized that the poor results obtained in applying the data of Lim et al. to existing correlations could also indicate that those correlations were not suitable for mixtures in the region of high values of viscosity and density. The data resulting from this experimental program for methane and propane have been reported by Huang et al. (*8*), and those for mixtures of methane and propane are the subject of this paper.

APPARATUS AND MATERIALS

The apparatus used in this investigation is the same as that reported by Huang et al. (*8*) except for the method of pressure measurement in the viscometer and the equipment used to prepare the mixtures.

A differential pressure indicator of the type described by McCreary and Swift (*11*) was used, in conjunction with a Heise Bourdon tube gauge, to determine the pressure in the viscometer. By installing the differential pressure indicator, it was possible to confine the experimental mixture within the controlled temperature environment, thereby making it possible to insure that the mixture was maintained in a single-phase condition at all temperature levels investigated. The differential pressure indicator-Heise gauge combination was calibrated with a pressure balance accurate to at least ± 1 lb./sq.in. The calibration indicated that the maximum uncertainty in the pressure measurement at any of the pressure and temperature levels investigated in this study was ± 15 lb./sq.in. The uncertainty of temperature measurement and control in the viscometer apparatus for this study was the same as that reported by Huang et al.

The equipment used for the preparation of mixtures consisted of two precision bore, variable volume cylinders, a differential pressure indicator, and appropriate manifolding and valves, all of which were enclosed in a well-stirred oil bath maintained at 37.8° ± 0.1°C. Pressures in this equipment, measured by the differential pressure indicator-pressure balance combination, had a maximum uncertainty of ± 1 lb./sq.in. This equipment, in addition to being used for the preparation of mixtures, was used to displace measured volumes of fluid mixture into the viscometer for the purpose of determining mixture densities.

The viscosity data of this study were determined with the No. 2 falling cylinder. The method of calibration and the data of calibration for this falling cylinder were reported by Huang et al.

Phillips pure grade methane and instrument grade propane were the starting materials used for the preparation of mixtures. The analyses reported by Huang et al. are appropriate since the materials for this study were taken from the same storage cylinders and had been subjected to the same procedure for removing water and carbon dioxide.

Mixtures were prepared volumetrically. A known volume of each starting material, measured at a specified temperature and pressure, was displaced from the pure component displacement cylinder to the mixture equilibration cylinder. The resultant mixture was allowed to equilibrate for at least 33 hr. at a pressure greater than the cricondenbar pressure of the mixture (*14*). Subsequent displacements of mixture into the experimental apparatus were conducted at pressures higher than the cricondenbar pressure. Mixture compositions were computed by converting the displaced volumes of starting materials to masses by using the density data of Sage and Lacey (*16*). Error analysis indicated that this procedure for preparing mixtures resulted in maximum errors of ± 0.005 mole fraction, including the changes of methane density due to the presence of nitrogen. Although the precision of chromatographic analyses was not this good because of the nature of this type of analytical equipment, statistical analysis of samples analyzed indicated that the results of the error analysis were correct. That a homogeneous mixture was indeed achieved after 33 hr. of equilibration was verified by noting that no change in pressure occurred at constant volume and constant temperature at times in excess of 33 hr. and replicated viscosity and density data obtained for a given mixture at the end of approximately 150 hr. agreed well with those taken 33 hr. after the mixture was prepared.

A complete description of the apparatus, method of preparing and analyzing mixtures, calibration, and error analysis is given by Huang (*7*).

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EXPERIMENTAL RESULTS AND DISCUSSION

Experimental viscosities and densities were determined for three methane-propane mixtures. Measurements were performed for the 22.1 and 50.0 mole % methane mixtures at pressures to 5,000 lb./sq.in.abs. over the temperature range from −120° to 37.78°C., and for the 75.3 mole % methane mixture at pressures to 5,000 lb./sq.in.abs. over the temperature range from −150° to 37.78°C.

Tables 1, 2, and 3 present recommended values of viscosity and density for the 22.1, 50.0, and 75.3 mole % methane mixtures, respectively. The tabular information presented was obtained from smoothed curves of viscosity and density as functions of pressure with temperature as a parameter. The curves from which the tabulated values were read agreed with the experimental values within ± 1%, except for the density values reported at pressures less than 2,000 lb./sq.in.abs. In this case the curves were obtained by extrapolating the high-pressure, experimental, density data to the bubble point pressures (*1, 13, 14*) by using the density data of Sage and Lacey (*16*) at 37.78°C. as a guide.

Experimentally determined viscosities for methane and propane previously reported (*8*) and for the three mixtures of this investigation at −100°C. are plotted as a function of composition in Figure 1. The data, plotted in this manner, indicate consistency between data determined for the pure components and those for the mixtures (different falling cylinders were used) and also give additional verification of the validity of the method used to prepare mixtures. The data of Lim et al. (*10*) for the methane-propane systems at −100°C. are also presented in Figure 1 for comparison. The data of that study for the 76.7 mole % methane mixture are in agreement with the data reported in this paper, while those obtained for mixtures containing 53.6 and 27.9 mole % methane are not in agreement. This is to be expected since the equipment used by Lim et al. did not make special provision to maintain a single-phase condition of the fluid under study by completely isolating the fluid in the viscometer. Failure to do so would be of more significance in the mixtures containing less methane where the cricondentherm temperature goes above ambient temperature.

The reproducibility of the viscosity measurements from different runs and from different preparations of the same composition mixture was within ± 2.0%. The viscosity data of this study at 37.78°C. were compared with those of Giddings (*5*) and of Bicher and Katz (*2*). Agreement with the data of Giddings was, on the average, within ± 2%, while the data of Bicher and Katz, which were determined by the rolling ball viscometer, were consistently lower than those of this study. The reproducibility of density measurement in this study was within ± 0.8%, and the agreement with the data of Sage and Lacey (*16*) at 37.78°C. was within ± 1.2%.

Figure 2 shows a residual viscosity vs. density diagram constructed from the data of methane and propane (*8*) and from those of the three mixtures of this investigation. Molar density was used instead of mass density in the construction of this diagram, since the former gave a better presentation of the data of methane-propane system on a single diagram. The atmospheric pressure viscosities for the mixtures were calculated from those of the pure components (*7*) and the equation (*3*)

$$\mu_{0m} = (x_1 \sqrt{M_1}\, \mu_{01} + x_2 \sqrt{M_2}\, \mu_{02})/(x_1 \sqrt{M_1} + x_2 \sqrt{M_2}) \qquad (1)$$

In Figure 2 the data for pure methane and pure propane (5 and 1, respectively) show less scatter than those for the mixtures (2, 3, and 4). This is to be expected inasmuch as the density data for the mixtures have a greater uncertainty associated with them than do those for the pure components. The contrast between the pure component and mixture data representations in Figure 2 illustrates the sensitivity of the residual viscosity-density correlation to error in density in the dense-fluid region and indicates that correlations based upon this concept will have limited utility in the dense-fluid region.

Several correlations from the literature were tested (*7*) by using values of viscosity and density for methane and propane previously reported (*8*) and those for mixtures presented in this study. Of the correlations tested that of Golubev and Agaev (*6*), which is presented in Figure 3, gave the most systematic representation of the data. For this correlation, the pseudo critical mixture densities were computed by the method of Prausnitz and Gunn (*12*):

$$\rho_{cm} = (x_1 M_1 + x_2 M_2)/(x_1 V_{c1} + x_2 V_{c2}) \qquad (2)$$

Table 1. Recommended Viscosity and Density Values for 22.1 Mole % Methane–77.9 Mole % Propane

	Temperature, °C.							
	37.78		0		−20		−40	
Pressure lb./sq.in.abs.	Viscosity, micropoise	Density, g./cc.	Viscosity, micropoise	Density, g./cc.	Viscosity, micropoise	Density, g./cc.	Viscosity, micropoise	Density, g./cc.
B.P.°	640	0.410	970	0.470	1,190	0.497	1,450	0.524
500	—	—	—	—	1,200	0.500	1,470	0.527
1,000	676	0.421	1,020	0.482	1,250	0.510	1,530	0.535
2,000	785	0.451	1,110	0.500	1,350	0.525	1,630	0.548
3,000	870	0.467	1,200	0.512	1,440	0.535	1,730	0.556
4,000	949	0.482	1,290	0.521	1,540	0.542	1,830	0.563
5,000	1,020	0.495	1,380	0.530	1,630	0.549	1,930	0.569
	−60		−80		−100		−120	
B.P.°	1,820	0.550	2,340	0.576	3,140	0.600	4,580	0.625
500	1,860	0.554	2,390	0.580	3,210	0.604	4,700	0.628
1,000	1,930	0.560	2,460	0.585	3,290	0.608	4,830	0.631
2,000	2,050	0.571	2,610	0.593	3,480	0.616	5,090	0.637
3,000	2,170	0.577	2,750	0.598	3,660	0.620	5,350	0.641
4,000	2,300	0.583	2,900	0.605	3,850	0.625	5,620	0.644
5,000	2,420	0.588	3,040	0.609	4,040	0.629	5,890	0.649

° Bubble point pressure values are from the literature (*1, 13, 14*).

Table 2. Recommended Viscosity and Density Values for 50.0 Mole % Methane–50.0 Mole % Propane

Temperature, °C.

	37.78		0		−20		−40	
Pressure, lb./sq.in.abs.	Viscosity, micropoise	Density, g./cc.	Viscosity, micropoise	Density, g./cc.	Viscosity, micropoise	Density, g./cc.	Viscosity, micropoise	Density, g./cc.
B.P.*	315	0.275	560	0.350	735	0.396	910	0.432
500	—	—	—	—	—	—	—	—
1,000	—	—	—	—	740	0.400	935	0.440
2,000	438	0.338	670	0.403	840	0.435	1,020	0.464
3,000	538	0.379	760	0.427	920	0.453	1,100	0.478
4,000	611	0.403	830	0.445	1,000	0.467	1,180	0.490
5,000	676	0.420	890	0.458	1,070	0.478	1,260	0.499
	−60		−80		−100		−120	
B.P.*	1,120	0.469	1,450	0.499	1,900	0.529	2,710	0.557
500	—	—	1,460	0.500	1,930	0.532	2,780	0.560
1,000	1,150	0.477	1,510	0.507	1,990	0.537	2,860	0.562
2,000	1,240	0.492	1,610	0.518	2,110	0.545	3,030	0.568
3,000	1,320	0.503	1,700	0.527	2,230	0.550	3,200	0.573
4,000	1,400	0.512	1,800	0.535	2,350	0.557	3,380	0.578
5,000	1,480	0.520	1,900	0.541	2,470	0.562	3,550	0.582

* Bubble point pressure values are from the literature (*1, 13, 14*).

where the critical molar volumes for pure components are from Rossini et al. (*15*), and the residual mixture viscosities at the pseudo critical point were defined by

$$(\mu_c - \mu_{c0})_m = x_1(\mu_{c1} - \mu_{c01}) + x_2(\mu_{c2} - \mu_{c02}) \qquad (3)$$

where critical viscosities and atmospheric pressure viscosities at critical temperatures for pure components are from the literature (*8, 17* to *19*). The experimental mixture data of this study are seen to be consistently above the correlation curve found by Golubev and Agaev. Furthermore, the mixture data are even above the dotted correlation curve which represents the best curve drawn through the pure component data for methane and propane (*8*). Better agreement could possibly be obtained for the mixture data in this correlation if more appropriate definitions for critical mixture densities and viscosities were used. This would not, however, alter the fact that the pure component data do not agree with the Golubev and Agaev correlation curve. For a complete discussion of the correlations tested by using the data of this study, refer to Huang's dissertation (*7*).

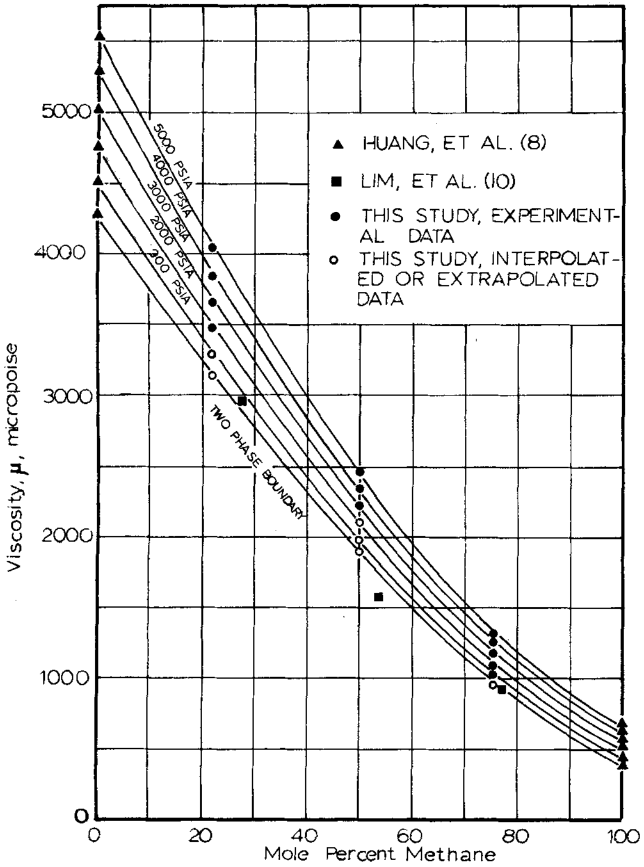

Fig. 1. Viscosity as a function of composition for the methane-propane system at — 100°C.

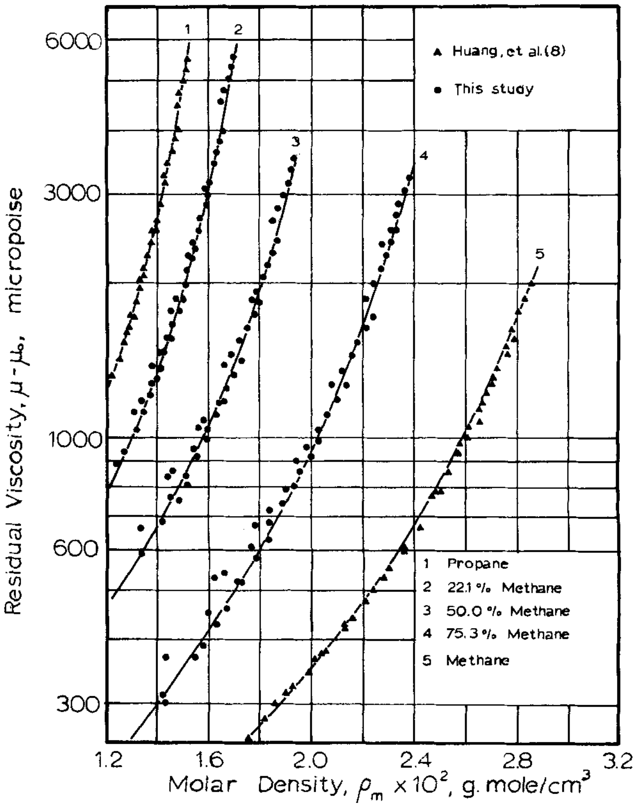

Fig. 2. Residual viscosity vs. molar density for the methane-propane system.

Table 3. Recommended Viscosity and Density Values for 75.3 Mole % Methane–24.7 Mole % Propane

	Temperature, °C.									
	37.78		0		−20		−40		−60	
Pressure, lb./sq.in.abs.	Viscosity, micropoise	Density, g./cc.	Viscosity, micropoise	Density, g./cc.	Viscosity, micropoise	Density, g./cc.	Viscosity, micropoise	Density, g./cc.	Viscosity, micropoise	Density, g./cc.
B.P.*	—	—	245	0.226	330	0.280	445	0.328	600	0.372
500	113	0.035	—	—	—	—	—	—	—	—
1,000	131	0.083	—	—	—	—	—	—	615	0.380
2,000	220	0.193	305	0.277	400	0.325	530	0.368	680	0.404
3,000	296	0.264	395	0.329	480	0.364	600	0.393	750	0.421
4,000	365	0.302	460	0.356	550	0.383	660	0.408	810	0.433
5,000	430	0.326	520	0.375	605	0.398	710	0.422	870	0.444
	−80		−100		−120		−140		−150	
B.P.*	740	0.408	960	0.446	1,330	0.478	1,920	0.507	2,440	0.522
500	745	0.410	975	0.449	1,360	0.482	1,980	0.510	2,510	0.526
1,000	785	0.422	1,020	0.455	1,410	0.487	2,050	0.514	2,600	0.529
2,000	860	0.437	1,090	0.467	1,510	0.495	2,190	0.520	2,760	0.533
3,000	930	0.448	1,170	0.474	1,600	0.500	2,330	0.525	2,930	0.537
4,000	990	0.458	1,250	0.482	1,690	0.506	2,460	0.530	3,100	0.542
5,000	1,060	0.467	1,320	0.490	1,780	0.513	2,600	0.535	3,280	0.546

* Bubble point pressure values are from the literature (*1, 13, 14*).

CONCLUSIONS

The viscosities and densities were determined for the 22.1 and 50.0 mole % methane mixtures at pressures to 5,000 lb./sq.in.abs. over the temperature range from −120° to 37.78°C. and for the 75.3 mole % methane mixture at pressures to 5,000 lb./sq.in.abs. over the temperature range from −150° to 37.78°C.

The reproducibility of the viscosity data was within ± 2%, and the agreement of these data with those reported by Giddings at 37.78°C. (5) was, on the average, within ± 2%. The reproducibility of the density data was within ± 0.8%, and the agreement of these data with those reported by Sage and Lacey at 37.78°C. was within ± 1.2%.

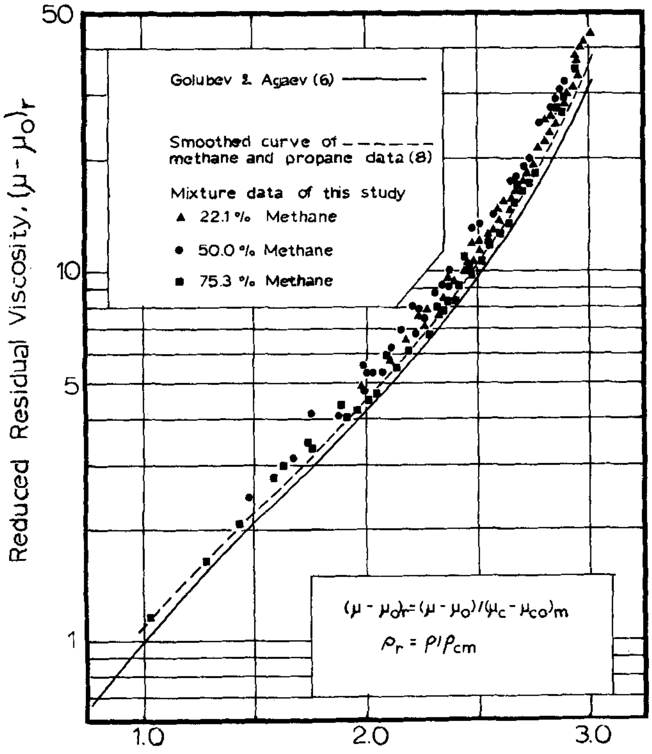

Fig. 3. Reduced residual viscosity vs. reduced density for the methane-propane system.

The data of this study were used to construct a residual viscosity vs. density plot. The higher uncertainty associated with the mixture densities is reflected on this plot as a marked increase in data scatter, illustrating the sensitivity of the residual viscosity-density correlation to error in density in the dense-fluid region.

A generalized reduced residual viscosity vs. reduced density correlation was prepared from the Golubev-Agaev approach. The degree of correlation was not considered to be satisfactory. Some improvement in the correlation could possibly be obtained by selecting more appropriate definitions for critical mixture properties.

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NOTATION

M_1 = molecular weight for methane
M_2 = molecular weight for propane
V_{c1} = critical molar volume for methane, cc./g.-mole
V_{c2} = critical molar volume for propane, cc./g.-mole
x_1 = mole fraction for methane
x_2 = mole fraction for propane

Greek Letters

μ = viscosity, micropoise
μ_0 = atmospheric pressure viscosity, micropoise
μ_{01} = atmospheric pressure viscosity for methane, micropoise
μ_{02} = atmospheric pressure viscosity for propane, micropoise
μ_{0m} = atmospheric pressure viscosity for mixture defined by Equation (1), micropoise

μ_{c1} = critical viscosity for methane, micropoise
μ_{c2} = critical viscosity for propane, micropoise
μ_{c01} = atmospheric pressure viscosity at critical temperature for methane, micropoise
μ_{c02} = atmospheric pressure viscosity at critical temperature for propane, micropoise
ρ = density, g./cc.
ρ_m = molar density, g.-mole/cc.
ρ_{cm} = pseudo critical mixture density defined by Equation (2), g./cc.
ρ_r = reduced density, dimensionless
$(\mu_c - \mu_{c0})_m$ = residual mixture viscosity at the pseudo critical point defined by Equation (3), micropoise
$(\mu - \mu_0)_r$ = reduced residual viscosity, dimensionless

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On Thermal Conductivity of Liquids

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The Bridgman equation for thermal conductivity of liquids is examined and a relation between sonic velocity and latent heat of vaporization is given. A correlation based on the hole theory of liquids is presented. This correlation predicts thermal conductivity in the temperature range of —20° to +80°C. for sixteen liquids, and at 20°C. for fifty liquids with an average absolute deviation of 9.5 and 5%, respectively. The correlation is also applied to liquid metals.

A recent paper (*1*) has reviewed the different methods of predicting thermal conductivity K of liquids and shows that the percentage deviation in predicting K values to be about 11% with the proposed method (*1*) used, which is about the same error obtained with the method of Sakiadis and Coates (*1*).

The Bridgman equation for thermal conductivity

$$K = \rho\, c_p U_l L \tag{1}$$

modified as

$$K = 2.8 (N/V)^{2/3} k U_l \gamma^{-1/2} \tag{2}$$

is believed to predict K values with an error of 10% (*2*). Equation (2) has not been tested adequately to assess its usefulness. Another drawback is the requirement of $U_l = f(T)$, if K is to be predicted as a function of temperature.

It is shown here that the velocity of sound in liquids bears a distinct relationship to latent heats of vaporization to predict K values with Equation (2). Furthermore, it is recommended that the constant 2.8 in Equation (2) be changed to 2.4 for better agreement with experimental values.

RELATION BETWEEN VELOCITY OF SOUND AND LATENT HEAT OF VAPORIZATION

Eyring and co-workers (*3*), who are mainly responsible for developing the concept of molecular holes in liquids, represent the partition function of a molecule in the liquid by the expression

$$F_l = \frac{(2\pi\, mkT)^{3/2}}{h^3} v_f b_l e^{-E_0/RT} \tag{3}$$

where E_0 is taken to be the difference in energy, per mole, between the molecules in the liquid and in the gas at 0°K. It is assumed in the present work that E_0 can be replaced by E, and therefore it is approximately equal to ΔH. This of course reduces to ΔE at 0°K. With this, the Eyring equation for the ratio of free volume to the volume inhabited by a molecule becomes

$$\frac{V_f^{1/3}}{V^{1/3}} = \frac{CRT}{\Delta H} = \frac{U_g}{U_l} \tag{4}$$