

The absolute accuracy of the experimental data is estimated to be approximately $\pm 5\%$ with the major sources of error being the fluctuations in transfer differentials and variations in tube bore measurements.

By combining the data in Table I with the data on hydrogen sulfide solubility, it is possible to plot viscosity *vs.* temperature with hydrogen sulfide content as the parameter as shown in Figure 3. This is the method of presentation originally used by Fanelli (3), and some of Fanelli's data are included in Figure 3 for purposes of comparison. Figure 4 shows the solubility of hydrogen sulfide in sulfur as a function of temperature and pressure. The values for solubility at one atmosphere are those reported by Fanelli in 1949 (4).

An inspection of Figure 3 immediately reveals that dissolved hydrogen sulfide strongly suppresses the viscosity of elemental sulfur above 158°C., and also progressively shifts the region of maximum viscosity from 188°C. to higher temperatures (a characteristic of virtually all viscosity suppressants for sulfur). It is obvious that the viscosity values predicted from Fanelli's data of 1946 are significantly higher than those obtained in this study. As has been explained, this discrepancy is due to the fact that the nominal concentrations reported by Fanelli only repre-

sent the total amount of hydrogen sulfide added to the system and not the actual amount dissolved in the sulfur.

It is believed that the viscosity data obtained in this study are considerably more accurate and reliable than those that have been available in the past. The new data may be applied with confidence to the design of engineering systems in which hydrogen sulfide is used to control the viscosity of molten elemental sulfur at temperatures in the viscous range.

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Viscosity of Methane-*n*-Butane Mixtures

J. P. DOLAN, R. T. ELLINGTON,¹ and A. L. LEE
Institute of Gas Technology, Chicago, Ill.

Data are presented for methane-*n*-butane mixtures containing nominally 25, 50, 70, and 90 mole per cent methane. Each mixture is shown to have a viscosity field similar to that of a pure component and the data for each can be correlated by use of a residual plot. Use of molar densities in the residual plot is shown to simplify the presentation of the composition dependence of viscosity.

PREVIOUSLY REPORTED investigations have defined the viscosity behavior of ethane (11), propane (18), and *n*-butane (7) for significant ranges of pressure and temperature. Detailed studies of the viscosity behavior in the critical region for ethane, propane, and *n*-butane have been reported (17).

In this investigation, the objective was to obtain sufficient data on the viscosity of mixtures of methane and *n*-butane to permit study of the effects of composition on viscosity behavior. These data have been used in a definitive test of the applicability of the residual viscosity concept in correlating mixture viscosity data. The residual concept was used also to extrapolate the data on individual mixtures.

A search of the literature revealed only one previous investigation of the viscosity of a binary hydrocarbon system for an extensive pressure-temperature field. Bicher and Katz (2) presented values of viscosity for the pure components and mixtures in the system methane-propane. Pressures were between atmospheric and 5000 p.s.i.a. Temperatures ranged from 77°F. to 437°F. The accuracy claimed was $\pm 3\%$, average. These data were used in preliminary trials of several concepts and for comparison of behavior trends. No data were found on methane-*n*-butane mixtures.

¹ Present address: Sinclair Research, Inc., Tulsa, Okla.

APPARATUS AND MATERIALS

The viscometer employed in this investigation operated on the same principle as the instrument employed previously in pure component investigations (9, 18). As a normal operating procedure, check runs on nitrogen at several conditions were carried out before and after each experimental measurement of hydrocarbon systems to insure that the instrument behaved properly.

Auxiliary vessels and manifolding have been added to permit preparation and mixing of samples of specified composition. The sampling system has been modified to permit obtaining representative samples for analysis. The result of this change in installation is to completely isolate the test sample within the thermostat, thus eliminating the possibility of condensation or diffusion due to temperature gradients.

A schematic diagram of the complete system is shown in Figure 1. Samples were prepared by displacing a certain volume of each component from vessel B to vessel C at constant pressure and temperature. The volume of each component determines the mass and thus the composition of the sample. To mix the sample, the system exterior to vessel C is evacuated. The sample confined in vessel C is then flashed to fill the viscometer and vessel B. Mixing of

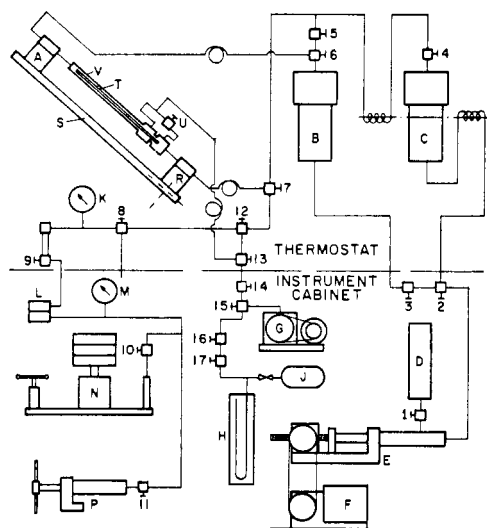


Figure 1. Schematic diagram, viscometer and auxiliary equipment

Vessels and equipment

- A. Viscometer instrument
- B. Stationary vessel
- C. Mixing vessel
- D. Mercury reservoir
- E. Mercury injection pump
- F. Electric motor for mercury pump
- G. Vacuum pump
- H. Manometer
- J. Sample bomb for mass spectrometer
- K. Estimating pressure gage
- L. Diaphragm separator
- M. Heise gage (0-10,000 p.s.i.g.)
- N. Deadweight gage (50-5,000 p.s.i.g.)
- P. High-pressure pump (5,000-10,000 p.s.i.g.)

Valves

- 1. Mercury reservoir control
- 2. Mixing vessel mercury control
- 3. Stationary vessel mercury control
- 4. Mixing vessel test fluid control
- 5. Stationary vessel test fluid control
- 6. Viscometer test fluid control
- 7. Viscometer test fluid control
- 8. Charging inlet control
- 9. Deadweight separator control
- 10. Deadweight gage control
- 11. Pressure pump control
- 12. Vacuum-sample system control from the manifold
- 13. Vacuum-sample system control from the viscometer
- 14. Vent valve
- 15. Vacuum pump control
- 16 and 17. Mass spectrometer sample high-pressure confinement cell

the sample is accomplished by displacing the sample back and forth between the two vessels on a path through the viscometer while maintaining a pressure that will keep the sample in a single phase. Movement of the sample is accomplished by displacement of mercury between the two vessels.

In the preparation of the methane-*n*-butane mixtures fluids of research grade were used without further purification. The *n*-butane was Phillips Petroleum Co. Research Grade, certified 99.9 mole % pure. The methane was obtained from the Southern California Gas Co. A typical analysis by mass spectrometer yielded 99.6% methane, 0.1% nitrogen, the remainder being ethane, propane, *n*-butane, and carbon dioxide. Analysis of completed mixtures showed that the ethane, propane, nitrogen and carbon dioxide were present in quantities not detectable by the mass spectrometer.

EXPERIMENTAL DATA

Data were obtained on four binary mixtures of the system methane-*n*-butane. This system was chosen due to the availability of density data (15, 16) and the possibility of more extensive study of the regions near the phase boundaries within the temperature limits of the present thermostat bath. The pressure and temperature ranges for the data are summarized in Table I. The calculated viscosity values and information pertinent to the calculation and correlation of data have been tabulated and deposited with the A.D.I.

Mixtures of desired compositions were prepared by volumetric displacement technique as described in the previous section. However, the mass spectrometer analysis of a series of samples showed a scatter in composition of $\pm 3\%$ with respect to the desired composition.

The approximate equation used to calculate the viscosity value from the experimental measurements (6) was used to estimate the uncertainty of the calculated value due to the uncertainty in the experimental measurements. In the liquid phase, i.e., temperatures below the critical and pressures well removed from the bubble point pressure, the uncertainty of the calculated value is $\pm 1.5\%$. The major contribution to this uncertainty is the composition effect.

In the gas phase the uncertainty of a viscosity value is $\pm 0.5\%$, with the equipment dimensions contributing all of the error. In regions of high gradients of density with pressure and temperature, the uncertainty is also $\pm 0.5\%$. In this last case the uncertainty is due to uncertainties in pressure and composition.

The plots of viscosity *vs.* pressure and viscosity *vs.* temperature, Figures 2 and 3, illustrate the general behavior of the mixtures. The estimated phase boundaries were obtained by extrapolating from higher or lower pressures to the dew- and bubble-point pressures. All data are shown by open symbols. Where isotherms or isobars of viscosity extend beyond the range of the data, construction from interpolated values was necessary. The interpolated values were obtained by use of the residual viscosity-density plots discussed below, in conjunction with the viscosity-pressure and viscosity-temperature plots. The effect of composition on viscosity is illustrated in Figure 4.

DATA TREATMENT

The concept of a transport property "residual" has its origin in the studies by Predvoditelev (14) of invariant quantities in heat transfer and liquid viscosity theory. Abas-Zade (1) applied the work of Predvoditelev to correlation of thermal conductivity data on liquids and vapors. The result of this application was that the residual thermal conductivity, defined as the thermal conductivity at the same temperature and a low pressure (atmospheric), at a given density was invariant with respect to temperature.

Table I. Temperatures and Pressure Ranges for Methane-*n*-Butane Data^a

Temp. ° F.	Pressure, P.S.I.A.	Temp. ° F.	Pressure, P.S.I.A.
25 Mole Per Cent Methane			
100	1000 to 2500	100	2000 to 4000
160	1000 to 2500	160	2000 to 3500
220	1250 to 2500	220	2000 to 3000
340	700 to 2000	280	600 to 3000
70 Mole Per Cent Methane			
100	1900 to 6000	70	2000 to 3000
160	1750 to 6000	100	600 to 8000
169	800 to 1825	160	600 to 3000
171	530 to 2000	220	800 to 5000
190	540 to 2500		
220	200 to 2500		

^aComposition uncertainty, $\pm 3\%$

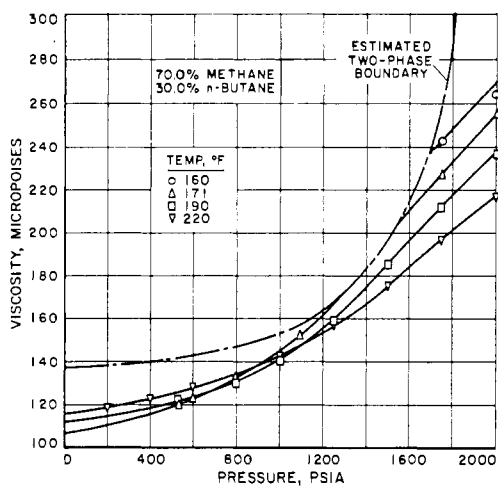


Figure 2. Gas phase region, 70 per cent methane, 30 per cent *n*-butane mixture

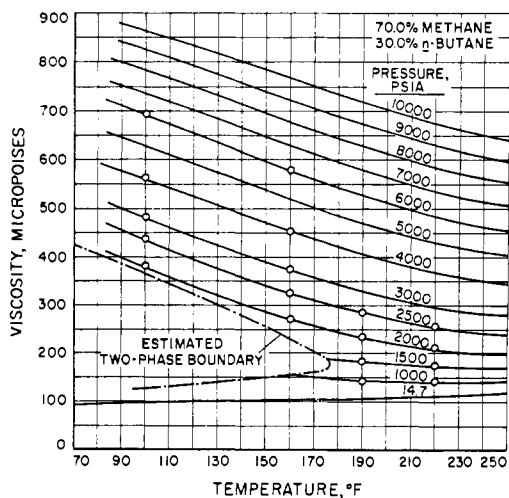


Figure 3. Viscosity vs. temperature, 70 per cent methane, 30 per cent *n*-butane mixture

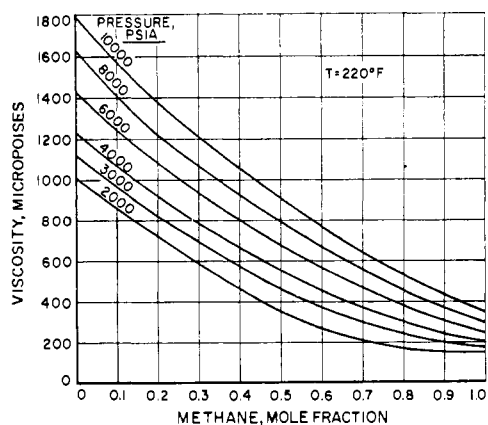


Figure 4. Viscosity vs. composition at 220° F.

This was proven by plotting residual thermal conductivity *vs.* density on log-log coordinates with a single curve representing all data. This type of plot was used by Brebach and Thodos (3) to correlate viscosity behavior. The correlation, plotted on linear coordinates, has been used successfully in previous investigations (7, 18) on pure components for checking the internal consistency of data, interpolation and limited extrapolation.

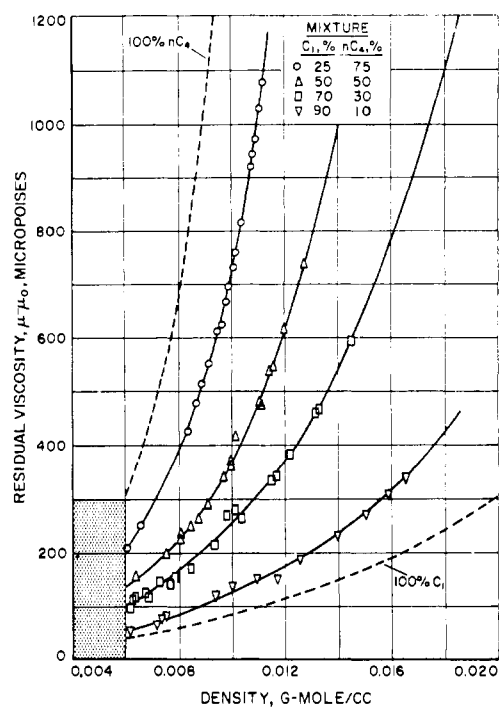


Figure 5. Residual viscosity plot of methane-*n*-butane mixtures, high density region

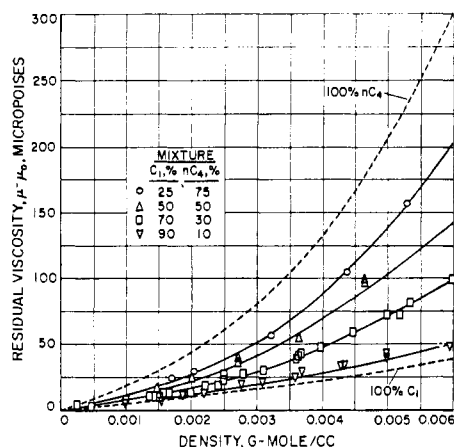


Figure 6. Residual viscosity plot of methane-*n*-butane mixtures, low density region

It was reasonable to expect that the data on a single homogeneous mixture could also be rectified by a residual plot. Exploratory tests with the data of Bicher and Katz (2) confirmed this.

Residual plots were employed successfully by Eakin and Ellington to ascertain and generalize molecular weight dependence for pure light hydrocarbons (8, 10). Therefore, it was logical that efforts be made to employ the concept to show composition dependence within a given system. On log-log plots, involving density, the available binary system data exhibited considerable disordering and intersection of constant composition lines. This might be expected from studies such as that of Hirschfelder and coworkers (13), to determine the conditions necessary for two-component gaseous systems to exhibit viscosity maxima with composition. Molar bases are conventionally employed to determine molecular effects and so plots of residual viscosity *vs.* density in gram mole/cc. were prepared (Figure 5 and 6); linear coordinates were employed to avoid emphasizing the scatter of data at low densities. The pure methane data employed were those of Comings and Mayland (5) and the pure *n*-butane data, those of Dolan and coworkers (7).

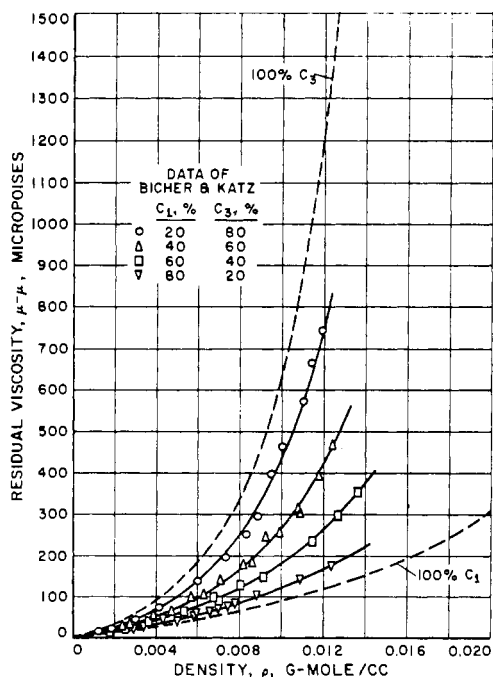


Figure 7. Residual viscosity plot of methane-propane mixtures

Several observations can be made on the basis of Figures 5 and 6. The effects of change of composition in the methane-*n*-butane system show regular trends between the limits of the two pure components. A plot of the methane-propane mixture data of Bicher and Katz (2), utilizing the propane data of Starling, Eakin, and Ellington (18) and the methane data of Comings and Mayland (5), Figure 7, yielded similar results. Possibilities for development of empirical mixing rules are immediately evident; one would be a fit to the curves obtained by cuts at constant density. It is felt that the residual plot using molar densities can be employed to estimate the viscosity of other methane-*n*-butane mixtures with reasonable accuracy and augment the other correlations available. It should be mentioned that a proven method for estimating the atmospheric pressure viscosity values exists (4). This method employs a mixing rule developed by Herning and Zipperer (12) and atmospheric pressure information on the pure components. This mixing rule has the form

$$\mu_m = \frac{\sum x_i \mu_i (M_i)^{1/2}}{\sum x_i (M_i)^{1/2}}$$

The pure component viscosities μ_i can be determined by the Sutherland Equation

$$\mu = \frac{BT^{3/2}}{T+S}$$

with appropriate constants, B and S . For the purpose of this investigation the Sutherland constants for methane, ethane and propane were those of Trautz and Sorg (19). The constants for *n*-butane were determined from the data of Dolan and coworkers (7). The Herning and Zipperer equation had previously been tested on light natural gases (4). The authors tested the mixing rule on the methane-

propane data of Trautz and Sorg; it reproduced the data with an average deviation of $\pm 0.5\%$.

SUMMARY

The data produced by this investigation serve to define the effect of composition on viscosity in the methane-*n*-butane system. The region covered is from 100 to 10,000 p.s.i.a. for temperatures from 100° to 460° F. It has been demonstrated that the concept of residual viscosity correlates the behavior of mixtures as well as it does data on pure components.

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NOMENCLATURE

- B = Sutherland constant
- M_i = Molecular weight of the i^{th} component
- S = Sutherland constant
- T = Temperature, ° R.
- μ = viscosity, micropoise
- μ_m = viscosity of the mixture, micropoise

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