A GENERAL VISCOSITY CORRELATION

FOR LIQUID MIXTURES

by

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PREFACE

This study is concerned with evaluating existing and formulating new correlations for the viscosity of binary mixtures of paraffin hydrocarbons. Viscosity of the n-butane-n-decane system was measured over a 25 to 85 mole fraction range to evaluate a correlation using logarithm of surface tension and reciprocal viscosity.

The surface tension correlation was judged invalid and other correlations from the literature were tested with experimental and literature viscosity data. A new correlation was devised using an experimentally-determined interaction parameter.

I wish to thank my major adviser, Dr. Robert N. Maddox, for his patience and concern during my research. Several other graduate students helped me considerably and I would like to thank them: Stuart E. Bennett, for designing and constructing the apparatus and for drawing details of it; James R. Deam, for his surface tension data and correlation, and his density data; William R. Owens, for his assistance in writing computer programs; and Harry G. Rackett, for his density and other equations. Much gratitude must go the sponsoring organizations, the Natural Gas Processors Association, who funded the research, and the National Aeronautics and Space Administration, who provided for my subsistence.

Last, but not least, I thank my wife, Jan, for helping me prepare this thesis and giving moral support during graduate school.

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CHAPTER I

INTRODUCTION

The Natural Gas Processors Association (NGPA) of Tulsa, Oklahoma, is sponsoring research on absorbers to determine causes for low efficiency and ways to improve this efficiency. The research at the Oklahoma State University School of Chemical Engineering is in two phases - static and dynamic. Included in the static phase are the study of viscosity and surface tension of paraffin hydrocarbon mixtures. The dynamic phase is concerned with evaluating absorption factors, A, from operating absorbers.

$$A = L/KV \qquad\qquad (1\text{-}1)$$

where

L = liquid flow rate, moles/hr

V = vapor flow rate, moles/hr

K = vapor-liquid equilibrium constant

Deam (6) has measured surface tension of pure components and liquid mixtures using a pendant drop apparatus. He has correlated these data with a parachor and an excess surface tension equation. For densities outside the range of literature data, he used the Rackett equation (30).

Bennett (2) designed and constructed a viscometer apparatus for use over a wide temperature and pressure range. Using a capillary

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viscometer, he measured the viscosity of liquid methane-n-nonane mixtures. He observed that plots of the logarithm of surface tension versus reciprocal viscosity generated a family of parallel straight lines of constant composition. This follows the work of Pelofsky (27) and Schonhorn (34), who used similar coordinate systems to correlate pure component viscosities. However, Bennett could not get a wide enough composition range using the methane-nonane system to fully test his hypothesis.

This author used Bennett's apparatus to measure the viscosity of the n-butane-n-decane system over a 25 to 85 mole per cent butane composition range. He also used literature viscosities of the methane-n-decane (24), n-hexane-n-hexadecane (17), n-hexane-n-tetradecane (17), and n-hexadecane-n-tetradecane systems to test the Bennett and other correlations. Even though the log surface tension-reciprocal viscosity plots do yield parallel straight lines of constant composition (Figures 10, 11, 12), these lines do not lie between the pure component lines as they would if mixture surface tension were a simple function of composition and pure component viscosity. Therefore, this type of correlation was discarded and other types were applied. The most successful type of correlation attempted was

$$\ln \mu = x_1 \ln \mu_1 + x_2 \ln \mu_2 + f(x, T, G^E) \qquad (1\text{-}2)$$

where f is an experimentally determined function of composition, temperature, and the excess Gibbs free energy. This approach is from Grunberg and Nissan (15) and Gambill (12), who suggest that the deviation from Arrhenius' prediction

$$\ln \mu = x_1 \ln \mu_1 + x_2 \ln \mu_2 \tag{1-3}$$

is a function of exponential reciprocal temperature, composition, and constants in the Margules free energy equation. This type of correlation gives a predicted viscosity within five per cent of the experimentally determined value.

CHAPTER II

LITERATURE SURVEY

Several different topics were surveyed in the literature. Rather
than confuse the reader by presenting the survey in one mass, the
author attempted to group the results according to these topics.

Viscosity Correlations

In addition to the Bennett correlation, other methods of pre-
dicting mixture viscosity were sought. The main type of correlations
published were corresponding states, empirical, surface tension, three-
body model, and residual viscosity.

Stiel (36) presents a plot of $\mu \xi$ vs. ω for saturated pure
liquids at $T_r = 0.7$ and one of $\mu \xi$ vs. T_r for a gaseous mixture of
nitrogen-ethylene. Each curve suggests that the reduced viscosity is
a function of the independent variable, acentric factor and reduced
temperature, respectively. Stiel attributes the following rules to
Prausnitz and Gunn (36).

$$T_{cm} = \sum_i x_i T_{ci} \tag{2-1}$$

$$\omega_m = \sum_i x_i \omega_i \tag{2-2}$$

$$P_{cm} = (R\ T_{cm}/\sum_i x_i V_{ci})(\sum_i x_i Z_{ci}) \tag{2-3}$$

Stiel (36) also mentioned the work of Preston, Chapman, and

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Prausnitz (29), who have worked with the corresponding states principle in correlating the transport properties of cryogenic mixtures. They show that the reduced viscosity, η^*, is a function of reciprocal reduced temperature, $1/T^*$, alone, where

$$\log_{10} \eta^* = A + B/T^* \tag{2-4}$$

$$\eta^* = \eta\, r_o^{\frac{1}{2}}/(m^{\frac{1}{2}}\, \xi^{\frac{1}{2}}) \tag{2-5}$$

$$T^* = k\, T\, /\, \xi \tag{2-6}$$

Preston, et al. suggest mixing rules,

$$\xi_{12} = (\xi_1 \xi_2)^{\frac{1}{2}} \tag{2-7}$$

$$r_{o_{12}} = \tfrac{1}{2}(r_{o_1} + r_{o_2}) \tag{2-8}$$

$$m_{12} = 2\, m_1\, m_2/(m_1 + m_2) \tag{2-9}$$

$$\eta = \phi_1^2 \eta_1 + 2\, \phi_1 \phi_2 \eta_{12} + \phi_2^2 \eta_2 \tag{2-10}$$

$$\phi_j = \frac{x_j V_{cj}}{\sum_i x_i V_{ci}} \tag{2-11}$$

to use in reducing mixture data to a form suitable for the original correlation. The main value of this correlation is to calculate point values of viscosity and not a general line. One drawback of this system is the necessity of having experimental viscosity to determine η_{12}.

Gambill (12) lists several empirical equations proposed by others and makes comments about their applications. For miscible liquid-liquid mixtures, he separates the equations into two types, those with

and those without an interaction parameter. Equations with this parameter will predict experimental results more accurately than equations without, but generally this parameter must be determined using experimental results. Gambill says this parameter will vary with absolute temperature as exp(B/T), and will also be proportional with real-non-ideal mixtures to the energy of mixing.

Gambill (12) recommends equations by Kendall and Monroe (21) as the best equation without an interaction parameter

$$\mu_{1m}^{1/3} = x_1 \mu_1^{1/3} + x_2 \mu_2^{1/3} \qquad (2\text{-}12)$$

and Grunberg and Nissan (15) as the best with a parameter.

$$\ln \mu_{1m} = x_1 \ln \mu_1 + x_2 \ln \mu_2 + x_1 x_2 d \qquad (2\text{-}13)$$

Grunberg and Nissan (15) attached theoretical importance to their parameter by defining d as

$$d = C b \qquad (2\text{-}14)$$

where C is the ratio of the logarithm of the viscosity to the logarithm of the vapor pressure and b is the constant in the shortened form of the Margules equation:

$$\ln \gamma_1 = b x_2^2 \qquad (2\text{-}15)$$

In this way the interaction parameter can be calculated using the Van Laar equation with constants evaluated from van der Waal's equation.

$$\ln \gamma_1 = A/(1 + A x_1/B x_2)^2 \qquad (2\text{-}16)$$

$$A = (b_1/R\,T)(\sqrt{a_1}/b_1 - \sqrt{a_2}/b_2)^2 \qquad (2\text{-}17)$$

$$B = (b_2/R\,T)(\sqrt{a_1}/b_1 - \sqrt{a_2}/b_2)^2 \qquad (2\text{-}18)$$

$$a_i = 27\,R^2\,T_{ci}^2/(64\,P_{ci}) \qquad (2\text{-}19)$$

$$b_i = R\,T_{ci}/(8\,P_{ci}) \qquad (2\text{-}20)$$

Assume for a first estimate, the Arrhenius equation for mixture viscosity, Equation (1-3), the Antoine equation for pure component vapor pressure,

$$\log_{10}P = A - B/(C + t) \qquad (2\text{-}21)$$

where t is temperature in degrees Fahrenheit, and that vapor pressure of a mixture can be averaged by mole fraction, and the final equation for the Grunberg-Nissan interaction parameter is

$$d = (\ln\gamma_1/x_2^2)\left(\sum_i x_i \ln\mu_i \Big/ \sum_i x_i P_i\right) \qquad (2\text{-}22)$$

An empirical equation using diffusivity was proposed by Buddenberg and Wilke (4) for the viscosity of gas mixtures.

$$\mu_m = \frac{\mu_1}{1 + \dfrac{x_2}{x_1}\dfrac{1.385\mu_1}{D_{12}\rho_1}} + \frac{\mu_2}{1 + \dfrac{x_1}{x_2}\dfrac{1.385\mu_2}{D_{12}\rho_2}} \qquad (2\text{-}23)$$

Herning and Zipperer are attributed by Dean and Stiel (7) to have presented a correlation using molecular weight.

$$\mu_m = \frac{\sum_i \mu_i x_i (M_i)^{\frac{1}{2}}}{\sum_i x_i (M_i)^{\frac{1}{2}}} \qquad (2\text{-}24)$$

Silverman and Roseveare (35) proposed a viscosity correlation based on surface tension with two empirical constants.

$$\sigma^{-\frac{1}{4}} = A/\eta + B \tag{2-25}$$

Pelofsky (27) surveyed the field of surface tension-viscosity correlations and proposed

$$\sigma = A \exp(B/\eta) \tag{2-26}$$

Written in logarithmic form,

$$\ln \sigma = \ln A + B/\eta \tag{2-27}$$

Equation (2-27) states that a straight line with slope B can be drawn intersecting the point where the viscosity becomes infinite at a surface tension value of A using natural logarithm of the surface tension and reciprocal viscosity as coordinates. This idea, using $\ln \sigma$ and $1/\eta$ as coordinates, is the basis of Bennett's correlation.

Bennett (2) proposed that lines of constant composition plotted on this coordinate system would be straight and parallel, and distributed between the pure component lines according to a function of the composition.

Schonhorn (34) modified Pelofsky's equation to extend it over the entire range of the liquid phase. This is done by introducing η_v, the viscosity of the vapor in equilibrium with the liquid so that the final equation is

$$\sigma = A \exp\left[-B/(\eta_1 - \eta_v)\right] \tag{2-28}$$

Equation (2-28) satisfies the boundary condition at the critical point,

$$\text{as } \sigma_1 \rightarrow 0, \ \exp\left[-B/(\eta_1 - \eta_v)\right] \rightarrow 0 \qquad (2\text{-}29)$$

At points outside of the critical region, Equation (2-28) reduces to Equation (2-26).

Residual viscosity is one correlation used by most publishers of viscosity data to show the accuracy of the data. This is defined as the viscosity at a given temperature and pressure minus the viscosity of the gas at the given temperature and a standard pressure, usually atmospheric. Plotting residual viscosity as a function of density generally gives a single curve independent of temperature. The shape of the curve is a function of the molecular weight of the fluid studied.

Giddings and Kobayashi (13) have published a family of curves of different molecular weight mixtures using residual viscosity and reduced density as coordinates. They also show a chart of dilute gas viscosity as a function of temperature and molecular weight.

Several workers have published equations for dilute gas viscosity, including

Lee and Eakin (22) $\qquad \mu_m = \dfrac{(7.43 + 0.0133 \ M) \ T^{3/2}}{T + 75.4 + 139 \ M} \qquad (2\text{-}30)$

Sutherland (10) $\qquad \mu = B \ T^{3/2}/(T + S) \qquad (2\text{-}31)$

Viscosity and Density Data

The Zeitfuchs-type capillary viscometer used in this study measures kinematic viscosity. The Bennett correlation (2) uses absolute viscosity, which is the product of kinematic viscosity and density. Therefore, the density of the butane-decane system must be

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known at the experimental points.

Reamer and Sage (32) reported density data of the n-butane-n-decane system from 100 degrees F to 460 degrees F and from bubble point to the critical point or maxcondentherm of the mixture. Rackett (30) has devised an equation for density of mixtures

$$V/V_c = Z_c^{(1-T_r)^{2/7}} \qquad (2\text{-}32)$$

which was used to calculate the density of the system at points outside the range of published data.

Viscosity data of mixtures other than n-butane-n-decane were sought to test correlations. Since most correlations used pure component viscosity, these data were also needed.

Pure component viscosity data were found at atmospheric pressure for n-butane (1, 25, 16), n-hexane (1, 14), n-decane (1, 9, 14, 16), n-tetradecane (1, 14), and n-hexadecane (1). Pure component viscosity data at elevated pressures were found for n-butane (5, 8, 33, 37) and decane (9, 23).

Mixture viscosity data were found for the methane-n-decane system (24), the hexane-decane system (9), the hexadecane-tetradecane system (17).

The most exhaustive compilation of physical properties of pure components is API Project 44 (1). This work was used extensively by the author for viscosity data at atmospheric pressure, as well as for pure component density, surface tension, and vapor pressure.

Lipkin, Davison, and Kurtz (25) have measured and tabulated absolute and kinematic viscosity and density data of pure propane, isobutane, and n-butane over a temperature range of -100 degrees F to

100 degrees F at atmospheric pressure.

Grunberg and Nissan (16) have measured and tabulated n-butane viscosity from -76 degrees F to 86 degrees F and decane from -4 degrees F to 176 degrees F, all at atmospheric pressure.

Giller and Drickamer (14) have also measured and listed viscosities for n-pentane from -136 degrees C to 20 degrees C, n-hexane from -98.5 degrees C to 20 degrees C, n-heptane from -93 degrees C to 20 degrees C, n-octane from -62 degrees C to 20 degrees C, n-decane from -33.1 degrees C to 20 degrees C, n-dodecane from -11 degrees C to 20 degrees C, and n-tetradecane from 4.5 degrees C to 20 degrees C, all at atmospheric pressure.

Methane and n-butane data were published by Swift, Lohrenz, and Kurata (37) over a pressure and temperature range of 85-675 psia and -220 to -118 degrees F for methane and 45-250 psia and 68 to 212 degrees F for n-butane.

Carmichael and Sage (5) present experimental and smoothed data for n-butane at 40, 100, 160, 280, and 320 degrees F at pressures up to 5000 psia.

Absolute viscosity data for gaseous and liquid n-and iso-butanes are presented by Sage, Yale, and Lacey (33) at 100, 130, 160, 190, and 220 degrees F and pressures from atmospheric to 2000 psia.

Dolan, et al. (8) published "recommended values" for the viscosity of n-butane at temperatures from 100 degrees F to 460 degrees F and 14.7 to 10,000 psia. These data represent the work of several researchers and are smoothed points rather than experimental.

Other researchers have investigated the viscosity of liquid n-decane. Lee and Ellington (23) present smoothed and experimental

viscosity and density data over a temperature range of 100 to 460

degrees F at pressures from 200 to 8000 psia. Their experimental work

was only to 340 degrees F; the points at 400 and 460 degrees F are

predicted by a residual viscosity correlation.

Lee, Gonzalez, and Eakin (24) published recommended and experi-

mental viscosity and density values for the methane-n-decane system

over the complete composition range at temperatures of 100 to 340

degrees F and pressures from bubble point to 10,000 psia. The

experimental data were taken at compositions of 30, 50, and 70 mole

per cent methane and at pressures up to 7000 psia. The balance of

the points were calculated by residual viscosity.

In 1935, Dow (9) followed up the work of Bridgman (3) in studying

the effect of pressure on the viscosity of liquids. Bridgman used

pure liquids and Dow worked with mixtures. Dow studied six mixtures

of organic liquids, including n-hexane-n-decane. He presents relative

viscosity data for pure n-decane at 30 and 75 degrees C at pressures

to 4000 psia. He used a falling ball type apparatus and defined

relative viscosity as $\log t/t_0$ where t is the time of fall at 30

degrees C and atmospheric pressure.

Heric and Brewer (17) measured the viscosity of 14 binary liquid

nonelectrolyte mixtures, among them hexadecane-hexane, tetradecane-

hexane, and hexadecane-tetradecane. All data are at 25 degrees C and

are assumed at 14.7 psia. The entire composition range is covered,

and values for weight, volume, and mole fractions, kinematic viscosity,

density, excess Gibbs free energy of activation of flow, and excess

volume at each point are listed.

Sources of Other Data

Vapor pressure data were found in Perry's and from API Project 44 (1). Where vapor pressure was to be calculated, as in a computer program, Antoine's equation was used, with constants from API 44 (1).

API 44 was also the source of surface tension data, and outside of this range Deam's equation (6) was used.

$$\sigma_{mix} = \sum_i x_i \sigma_i + \sigma^E \qquad (2\text{-}33)$$

The correlation of Buddenberg and Wilke (4), Equation (2-23), required diffusivity data. These were calculated by extrapolating the data of Reamer, Lower, and Sage (32) to the temperature region of the butane-decane study.

CHAPTER III

APPARATUS

The apparatus used was basically that built by Bennett (2) and

the reader is referred to his thesis for more complete details.

The heart of the system is a glass capillary viscometer of the

Zeitfuchs cross-arm type. Since the walls cannot stand a pressure

differential of any magnitude, a pressure cell was built to maintain

a negligible pressure drop across the viscometer. This cell was en-

closed in a temperature bath, which in turn was surrounded by a pro-

tective shield to help save the operator in case of any accident in

the cell. The other major section was the pressure distribution sys-

tem, used to introduce gas to the pressure cell.

Viscometer

The viscometer used was a model C-50 Zietfuch cross-arm visco-

meter manufactured by the California Laboratory Equipment Company

(Figure 1). The components of the viscometer were the reservoir,

cross-arm, capillary tube, and supports.

The reservoir held the liquid sample and the cross-arm carried

the sample from the reservoir to the capillary. Fine lines painted

on the reservoir and cross-arm tube walls were used to insure a con-

sistent size sample for each run.

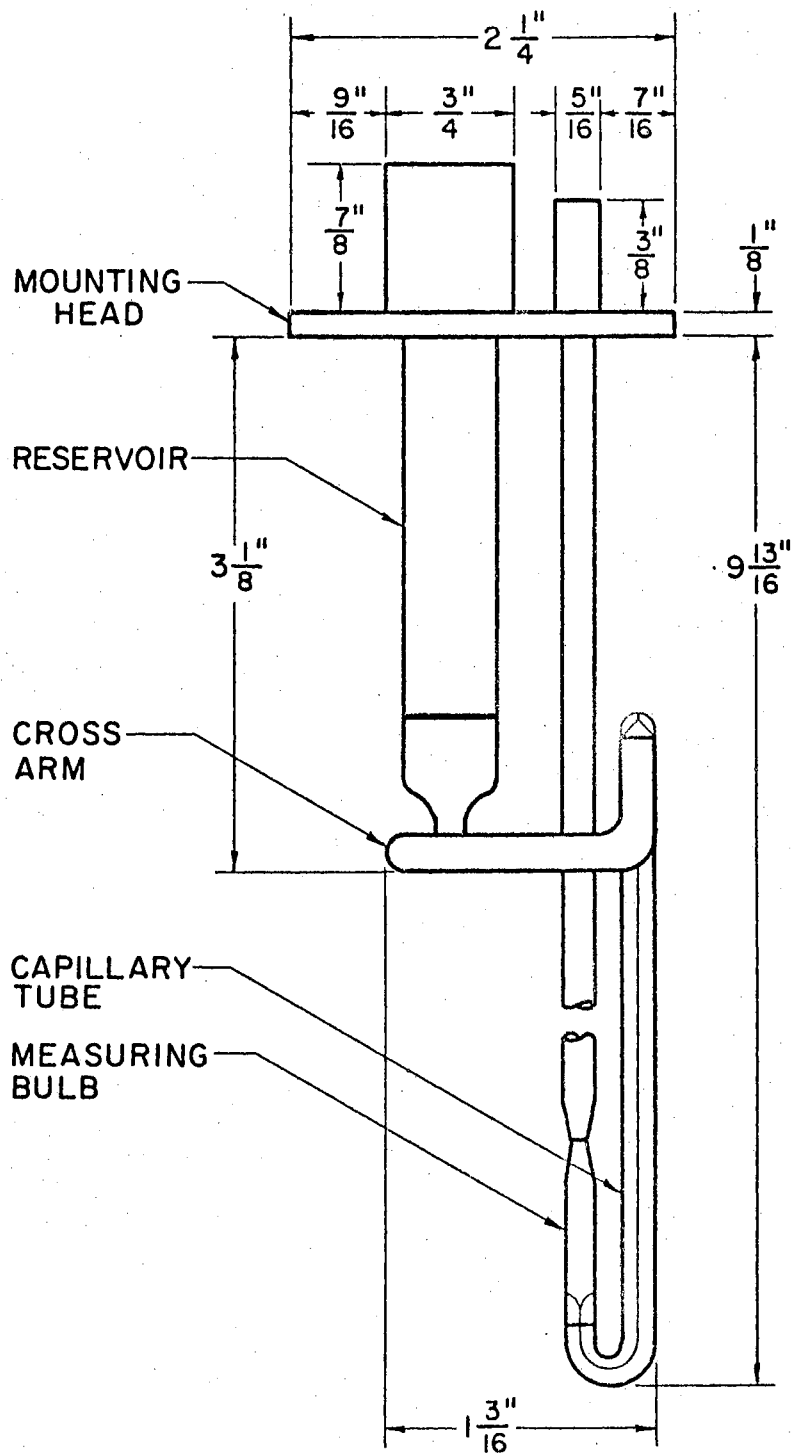In the capillary tube was a bulb with a fine line at the top and

Figure 1. Diagram of the Zeitfuchs Cross-Arm Viscometer

bottom. By measuring the time taken by the meniscus to travel between lines, the relative viscosity was known. Multiplication of the relative viscosity by the viscometer constant gave the kinematic viscosity of the sample.

The viscometer was connected to the liquid injector and methane feed lines by a "Teflon" sleeve fitted tightly against the walls of the reservoir and a length of "Tygon" tubing fitted tightly over the capillary end to the viscometer (Figure 5). A wing nut positioned the viscometer correctly on the sleeve. Slots cut vertically on the sleeve let gas escape from the reservoir to the pressure cell to maintain a zero pressure differential across the viscometer.

Pressure Cell

The pressure cell (Figure 2) maintained pressure on the visco-meter and allowed visual observation of the viscometer reservoir, cross-arm tube, and capillary bulb. Attached to the cell at the top was the liquid injection system.

The cell body (Figure 3) was a heavy stainless steel cylinder with observation ports and a top. The seal between the cell and the top was insured with a "Viton" O-ring when the top was bolted on.

Four 1¼ inch-diameter observation ports (Figure 4) were installed in the side of the cell. Each port was in four parts, the outer wall, retainer bolt, quartz window, and seals. The outer wall was a stain-less cylinder bored and threaded and welded to the cell wall. The retainer bolt was a hollow hex-head bolt used to hold the quartz window in place, tightened only hand-tight to prevent scratching the quartz. The window was a fused quartz lens made by the General
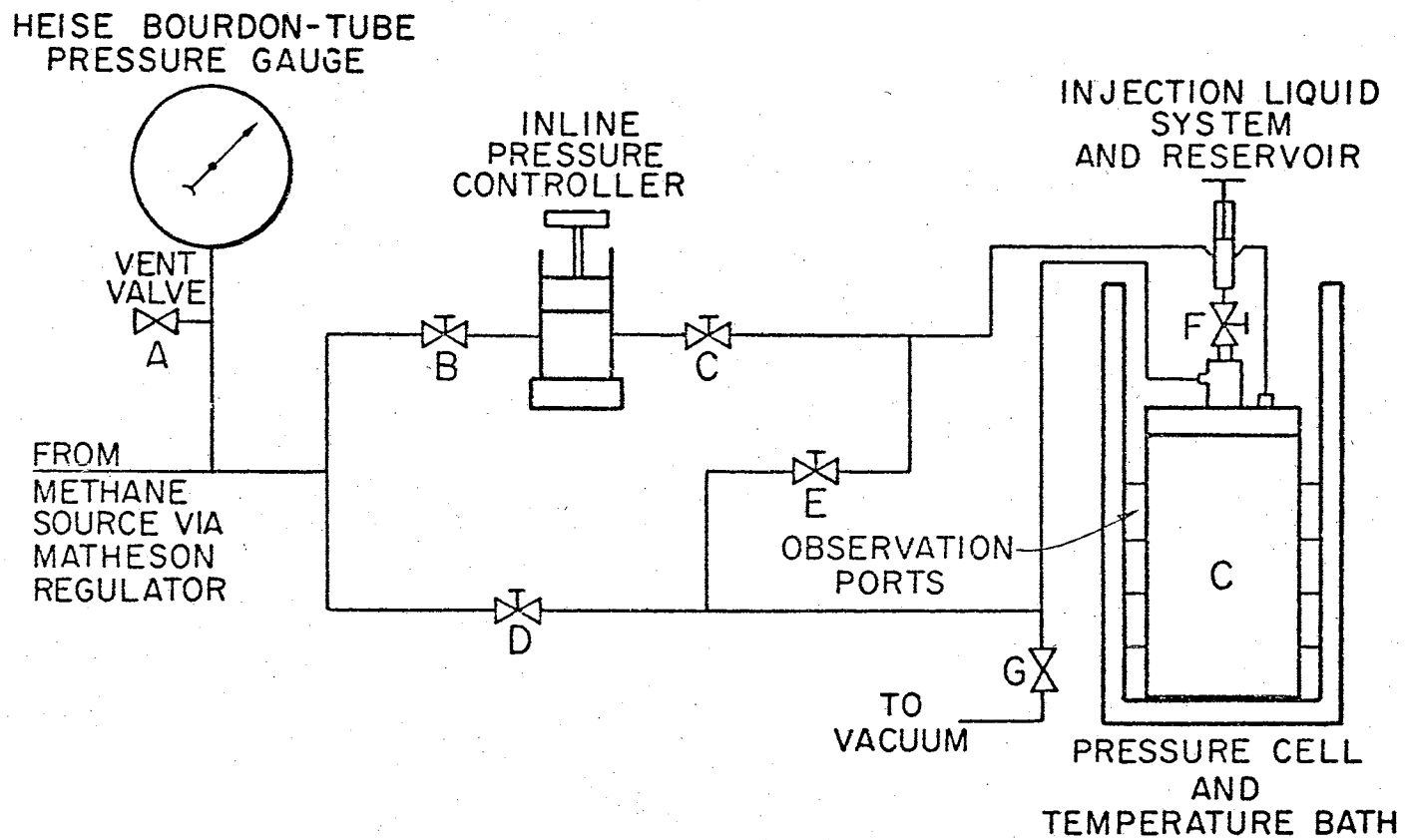
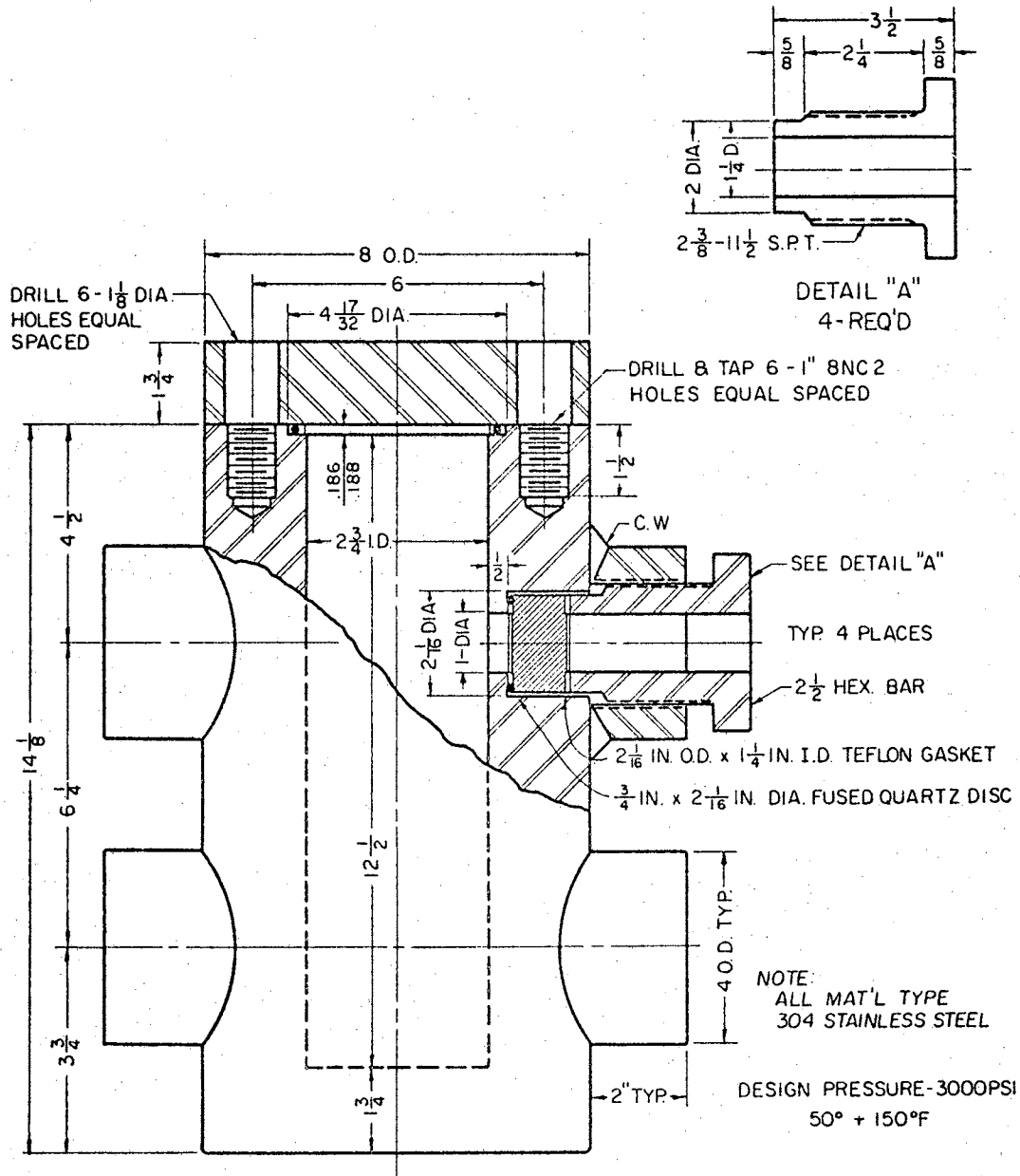Figure 2. Schematic Diagram of the Experimental Apparatus
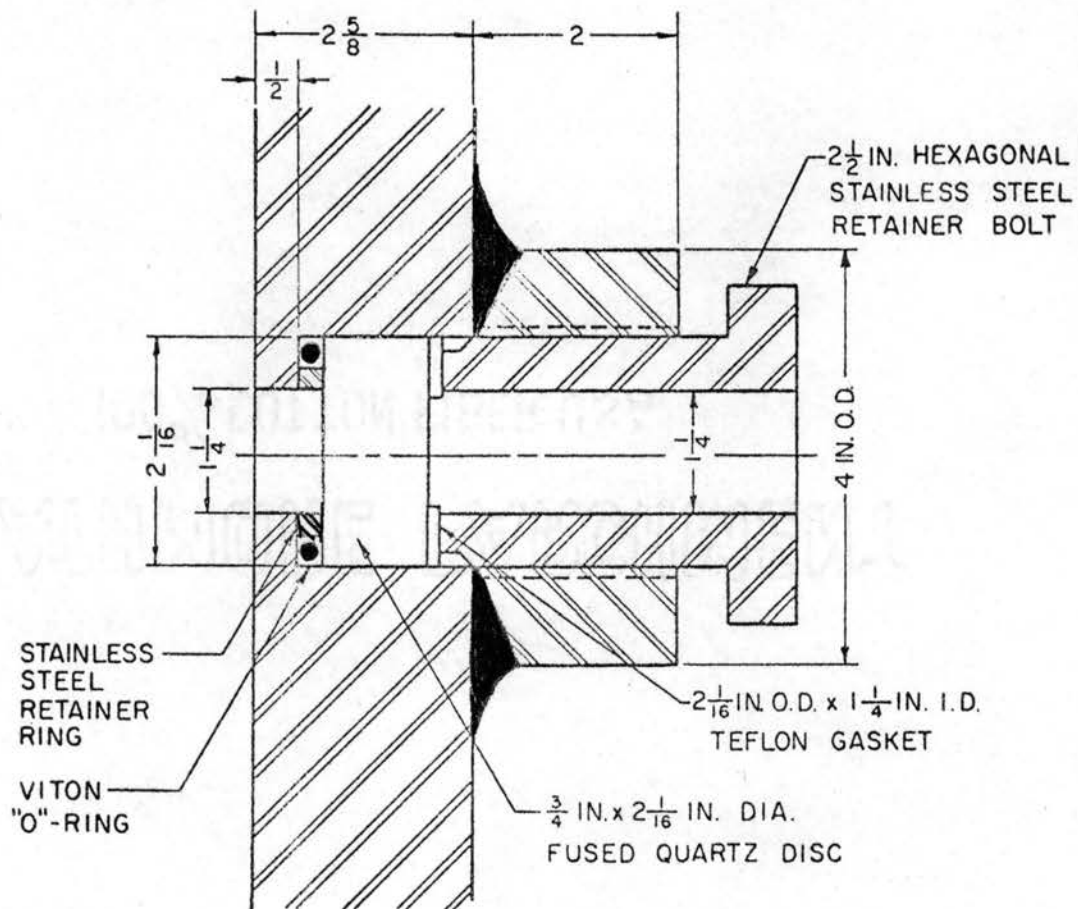
Figure 3. Detail of the Pressure Cell

Figure 4. Detail of the Observation Ports Assembly

Electric lamp glass department. The lenses were capable of service

to 2200 psia with a safety factor of seven to one. The seal between

the cell and the lens was achieved with a "Viton" O-ring with a

stainless steel ring inside to prevent collapse under vacuum. On

the other side of the lens was a "Teflon" gasket. Because of the

danger of the lens breaking, all observations were made by looking

at a mirror focused on the observation ports.

Liquid Injection System

The liquid injection system (Figure 5) held reserve liquid and

controlled the volume of liquid in the reservoir. The system con-

sisted of a liquid reservoir cylinder, injector piston, ball valve,

gas inlet, and a connection tube.

The reservoir held reserve liquid and the piston was used to

force this liquid into the viscometer reservoir or pull it back up.

The piston was operated by a screw driver. A ball valve was at the

base of the reservoir to hold the liquid in or out if a pressure

difference occurred between the reservoir and pressure cell.

Between the valve and the pressure cell were two concentric

areas. Attached to the annular area was a gas inlet and on the in-

side was a tube connecting the reservoir to the viscometer reservoir.

The lower tip of the tube was at the upper liquid level when the

correct volume was in the viscometer.

Temperature Controls

A temperature bath surrounded the pressure cell. Attached to

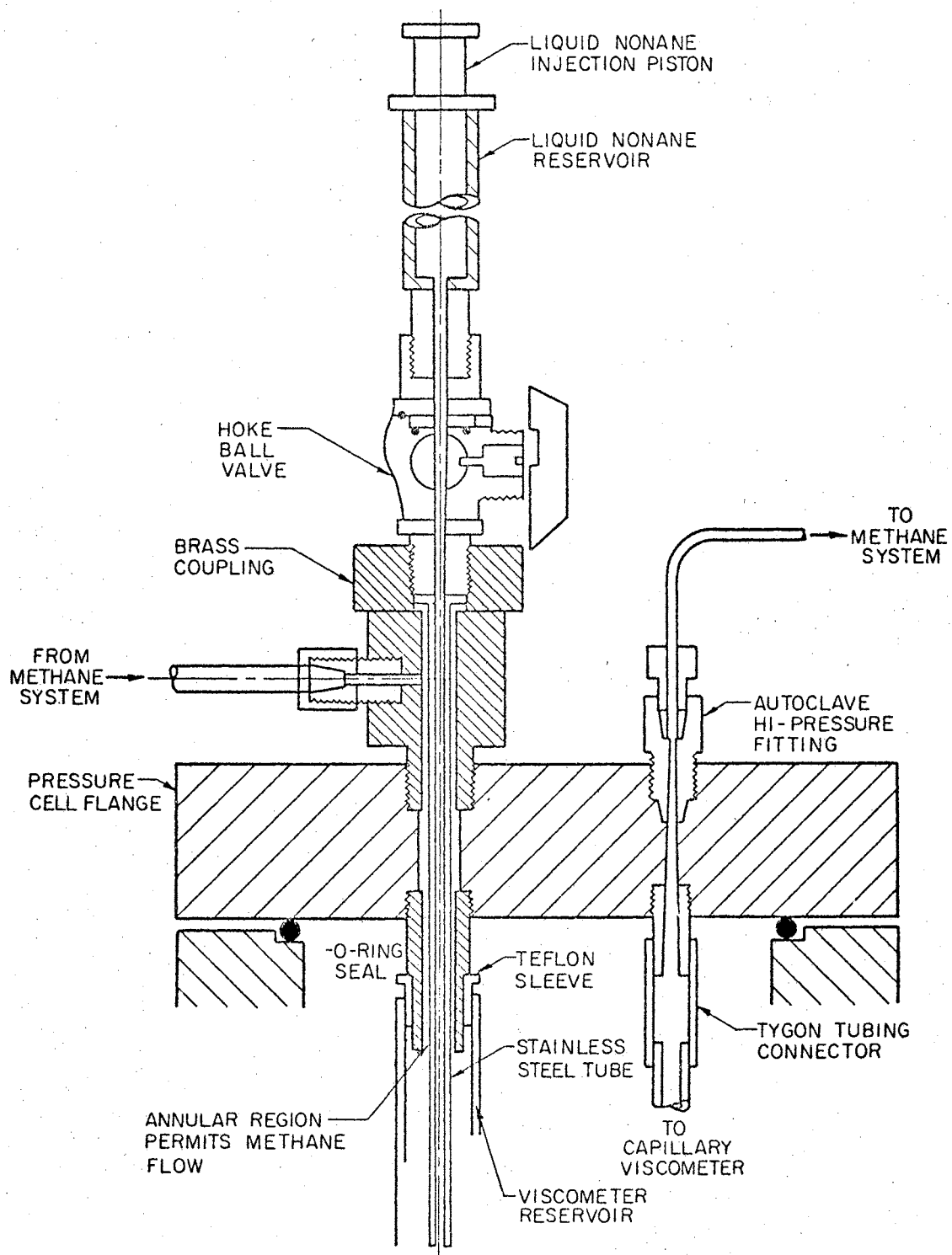the bath was a refrigeration unit circulating methanol as the heat-

Figure 5. Detail of the Liquid Injection Assembly

transfer medium. For runs at ambient or higher temperatures, the methanol was blocked off and water was put in the bath.

Due to the nature of this study, the only fluid used in the bath was water. For temperature lower than ambient, ice was used as the coolant. A heater system using a Lightnin' mixer, Calrod heater, Hallikainen Thermotrol, and Rosemount Engineering Co. temperature probe was used for other conditions.

The Pressure Distribution System

The functions of the pressure distribution system were to introduce the gas to the viscometer, control the level of liquid in the reservoir, and achieve fine control of the system pressure.

The gas used in this study was n-butane, which was stored in a cylinder adjacent to the unit. Bennett had used methane gas at pressures up to 1500 psia and had a Heise Bourdon-tube pressure gauge for measuring system pressure. This gauge was graduated in five psi increments up to 3000 psia and was unsuitable for use with butane, since the maximum pressure in a butane cylinder is 35 psia. An Ashcroft-American Duragauge graduated in one-half psi increments up to 30 psig and in one-half in Hg increments to 30 in Hg vacuum was mounted in parallel to the Heise gauge.

Pressure in the system was controlled by the regulator on the butane cylinder, the inline pressure controller and the vent valve (Figure 2). Major increases in pressure were achieved by adjusting the regulator, while fine changes were made with the inline pressure controller. The inline pressure controller was a cylinder with a piston attached to a screw drive. Changing the height of the piston

changed the volume and pressure of the system.

A Duo-Seal vacuum pump was used to evacuate the system before each run.

Materials Tested

The n-butane used was Phillips Petroleum Company Instrument Grade guaranteed to be at least 99.5 mole per cent butane. The n-decane used was Phillips Petroleum Company Research Grade guaranteed to be at least 99.85 mole per cent decane. Deam (6) also used these materials and analyzed them chromatographically. His results showed the printed analyses were correct.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The main steps in making an experimental run were charging the system, bringing the system to equilibrium, measuring viscosity, and dismantling the apparatus. Reference to Figure 2 will prove helpful while following the procedure.

Charging the system involved introducing the correct amount of liquid into the viscometer reservoir and filling the pressure cell with the gas studied. After the viscometer was attached to its holders on the top flange of the pressure cell and the ball valve shut, six to eight ml of liquid were pipetted into the injection reservoir and the screw driver given two or three turns to hold the piston in position. The top flange was bolted onto the pressure cell and the gas leads connected. The gas cylinder was hooked up to the systems. Vent valve A, the regulator valve, and the ball valve F were closed and all others open. The vacuum pump was turned on. After evacuation, valve G was closed and the pump shut off. The cylinder valve was opened and the system pressurized to 15 psia. Ball valve F was opened and the injection piston pushed down, forcing liquid into the system until the meniscus reached the line on the reservoir wall. Valves D, E, and F were closed. The regulator valve was slowly opened so bubbles were seen passing through the liquid in the reservoir. The bubbling continued slowly until the system was at the desired pressure

and the cylinder valve was then closed. The only valves used in equilibrating and running were B, C, D, and E. All others were closed. If viscosity was to be measured at a temperature other than ambient, the temperature bath was filled with the proper heat transfer medium and allowed to come to the correct temperature. When the system was at the desired temperature and pressure, it came to equilibrium. Gas slowly dissolved in the liquid naturally, but bubbling gas through it helped speed the process. The inline pressure controller was used to transfer the gas from the cell to the liquid. Valves B and D were opened and valve C closed. The controller piston was lowered, forcing gas through the capillary and the liquid. This was repeated once every thirty minutes for two hours until the system reached equilibrium.

Viscosity was measured by timing a specific volume of liquid as it passed through the capillary. Valves B, D, and E were closed and valve C opened. The piston was raised slightly, drawing liquid over the siphon into the capillary. The bulb was allowed to fill, wetting the walls. The piston was lowered until the bulb was empty. The piston was raised until liquid was drawn over the siphon again. Valve E was opened to equalize the pressure across the ends of the viscometer. Timing started as the meniscus passed the lower line and stopped as it crossed the top line. This time was reading number one. Valve E was closed and the piston lowered until the bulb was empty again. This was repeated nine times for each experimental point.

Bennett (2) showed there is no loss in accuracy to repeat the measurements with the same liquid when compared to using a new sample for each reading. If the wall of the viscometer is dry, the reading

will be different from one taken when the wall is wet. Therefore, the calibration must be done after the wall is wetted. Also all runs for record must be made with wet walls.

When all readings are complete, valves B, E, F, G, and the cylinder valve were closed and valves A, C, and D opened. The system was allowed to come to atmospheric pressure. The temperature bath was drained. The gas lines were then uncoupled and the top flange unbolted. The top should be lifted straight up so the viscometer will not touch the side of the cell. All sample liquid was drained from both reservoirs. Acetone was used to clean the viscometer, which was dried by gently passing dry air through it. The above procedure was repeated to make other experimental runs.

CHAPTER V

DISCUSSION OF DATA

The butane-decane system was chosen to study experimentally be-
cause Deam (6) had experimentally determined the surface tension and
density of the mixture at the conditions of this study. Also the
mixture was of two liquids and not of a gas dissolved in a liquid.

The procedure for determining the absolute viscosity of a sample
was to multiply the average time of a run by the density and the visco-
meter constant. The constant was determined by calibrating the visco-
meter with distilled water at 25 degrees C. Density was interpolated
from Reamer and Sage (32) or calculated by the Rackett equation (30), by
Deam's method (6), for points outside the experimental region (Figure 6).
The viscosity of each point was plotted on viscosity-composition charts
(Figure 7) and viscosity-temperature charts (Figure 8) to compare data
and use for possible correlation ideas.

The pressure and temperature range was limited by the apparatus.
The maximum pressure in a butane cylinder was 35 psia and the apparatus
could not be operated at pressure less than atmospheric. Raoult's Law
holds at these pressures and was used to determine the pressure-compo-
sition curve (Figure 9). The maximum temperature that could be reached
with the present heating system was 130 degrees F. In spite of these
limitations, the composition range from 0.25 to 0.85 mole fraction
butane was covered. The complete summary of experimental data appears
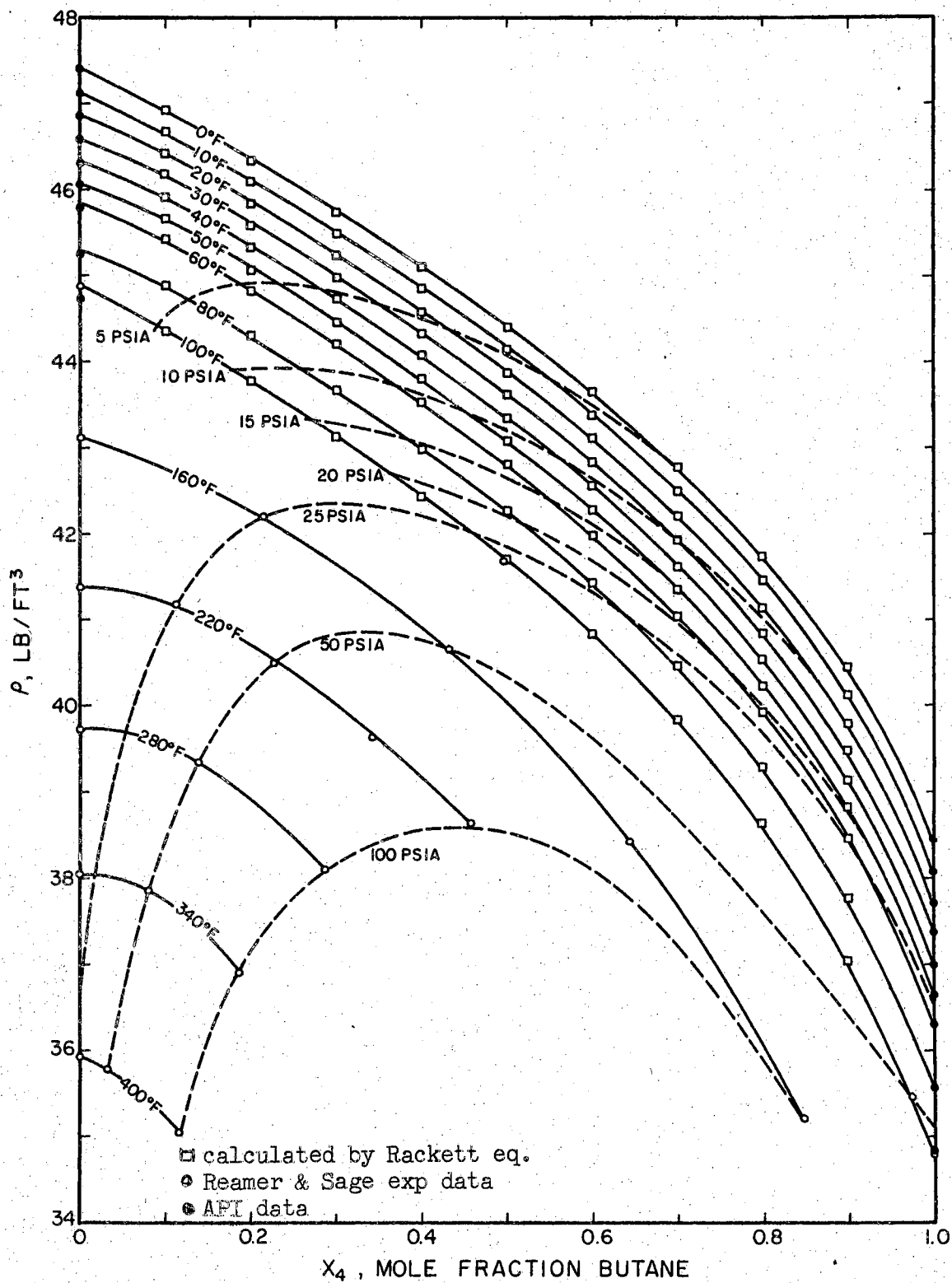as Table I.

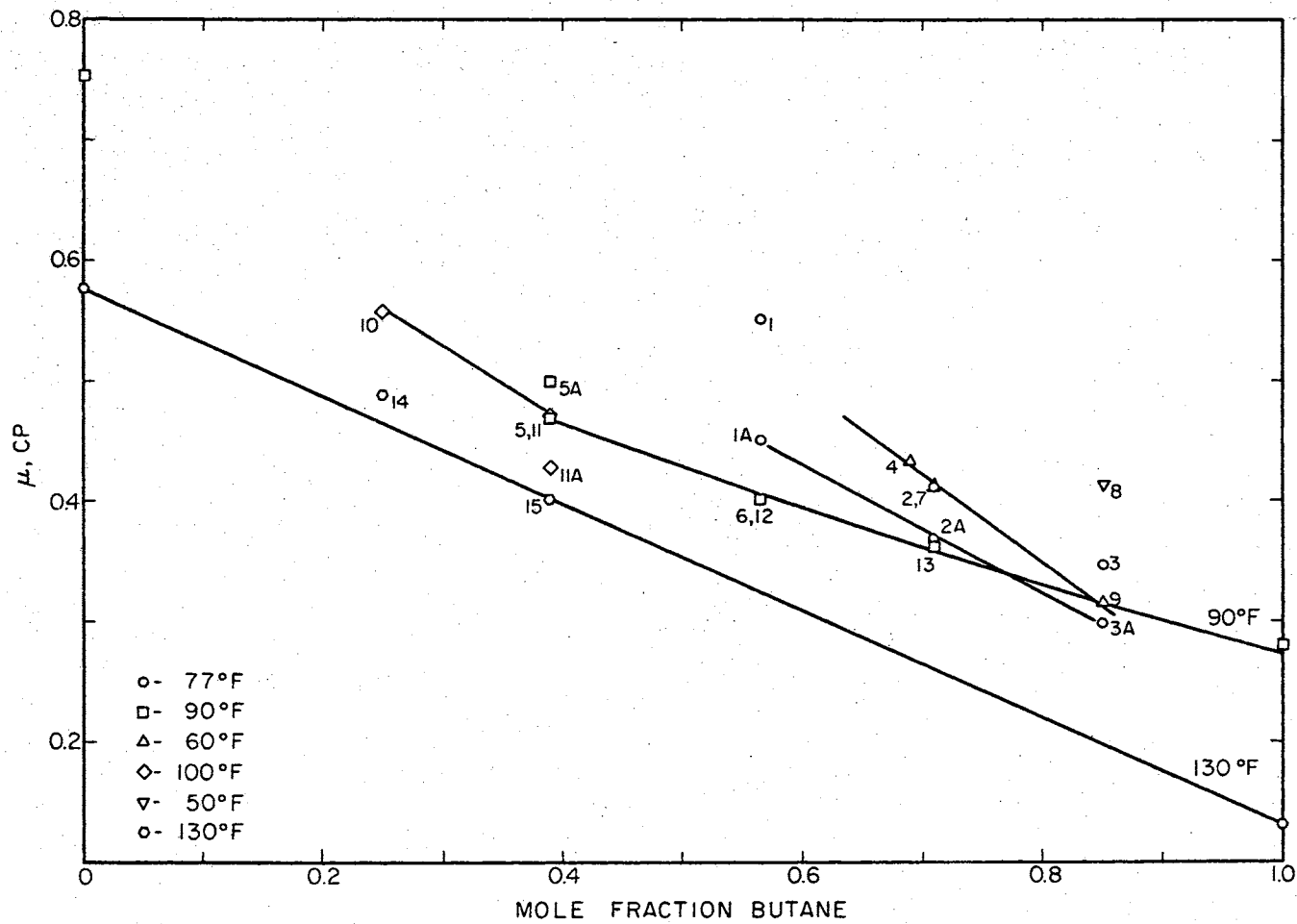Figure 6. Density of n-Butane-n-Decane Mixtures

Figure 7. n-Butane-n-Decane Viscosity-Composition Chart
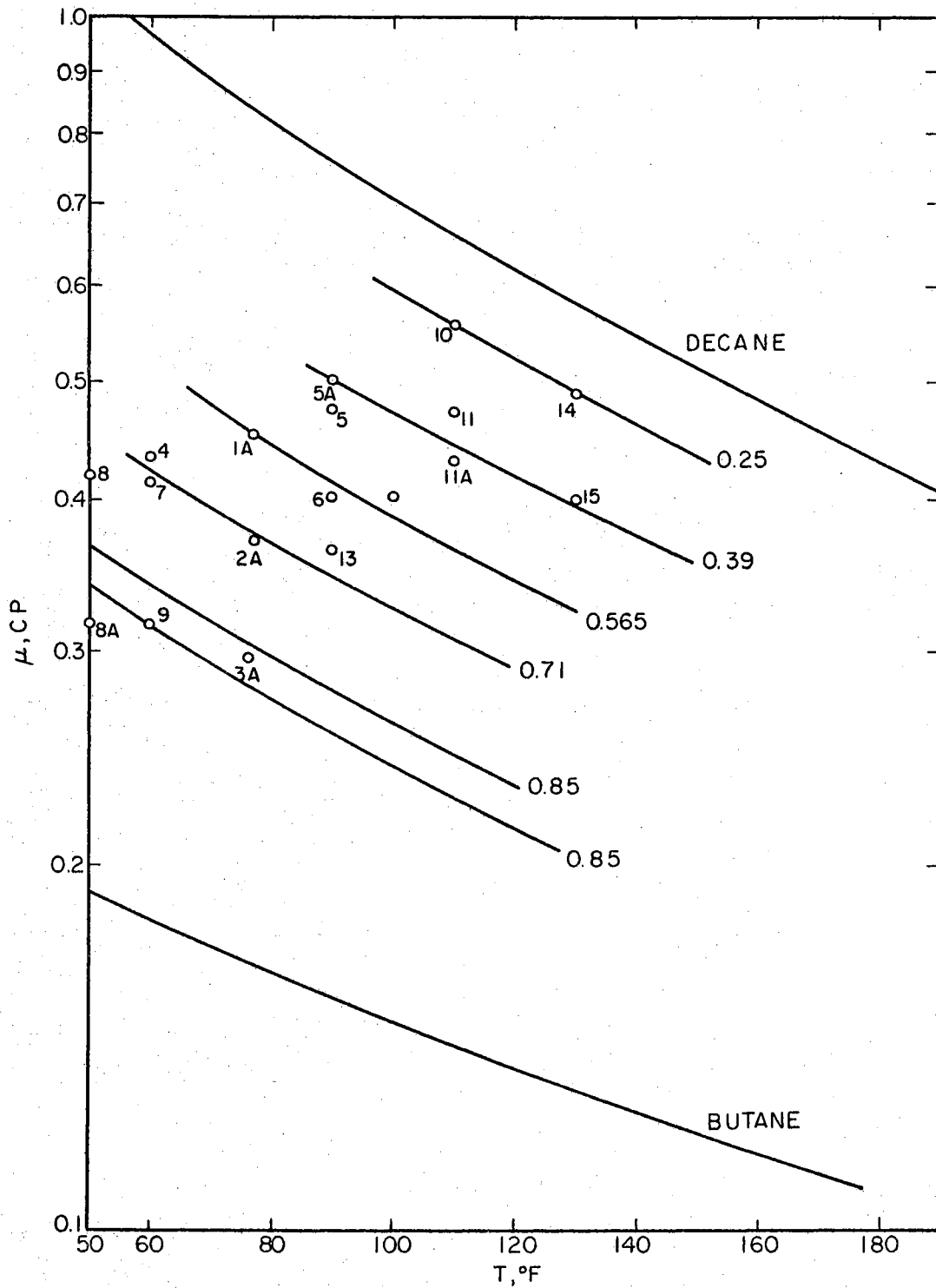
Figure 8. n-Butane-n-Decane Viscosity-Temperature Chart
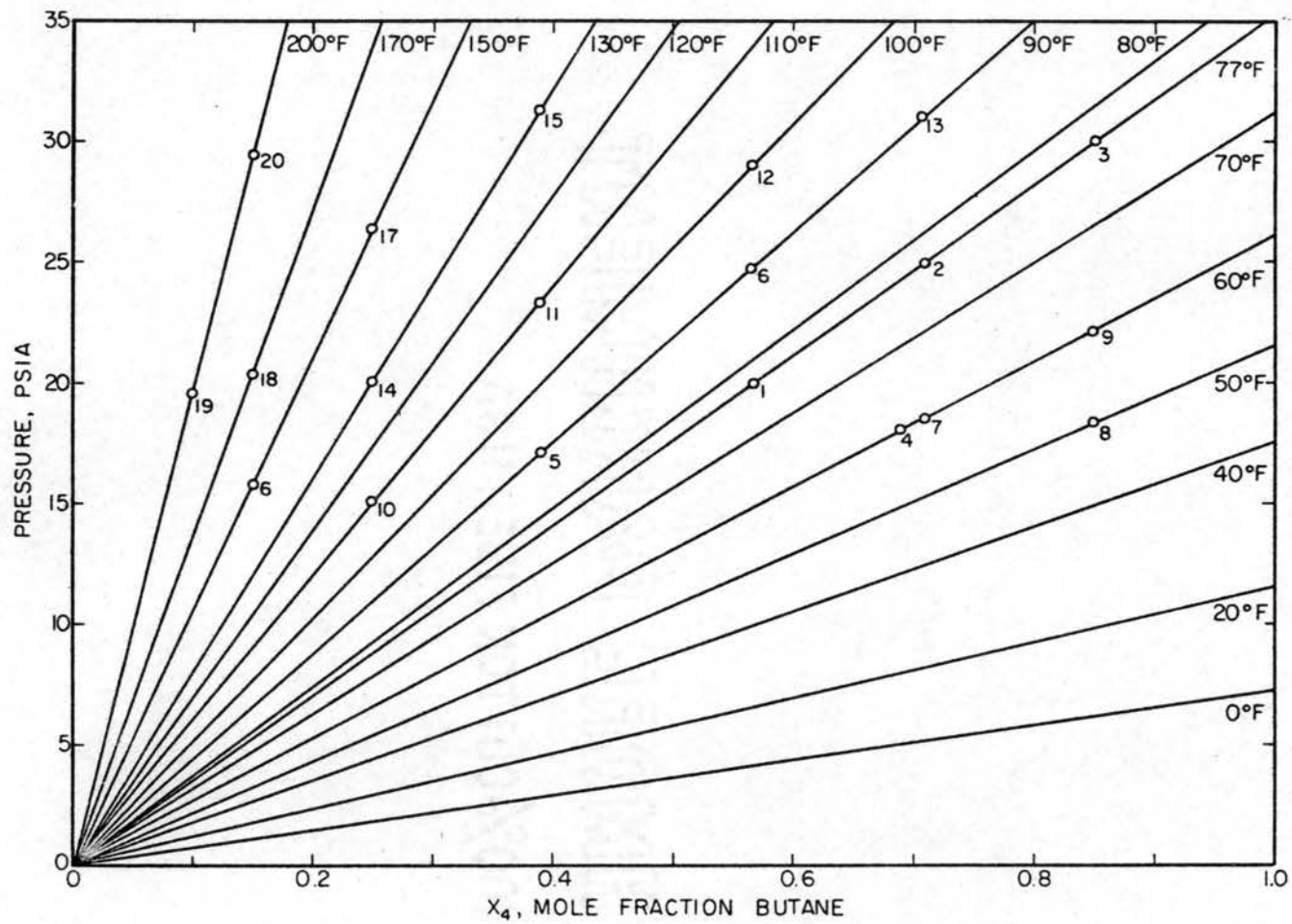
Figure 9. n-Butane-n-Decane Pressure-Composition Chart

TABLE I

SUMMARY OF EXPERIMENTAL DATA FOR BUTANE-DECANE

Run No.	Mole frac butane	T, Degrees F	Pressure psia	Density, gm/cm^3	Time, sec	Viscosity, cp
1	0.565	77	20.0	0.6696	77.5	0.4515
2	0.71	77	25.0	0.6471	59.8	0.3695
3	0.85	77	30.0	0.6183	52.8	0.2993
4	0.69	60	18.0	0.6592	61.7	0.4336
5	0.39	90	17.0	0.6856	64.9	0.4744
6	0.565	90	25.0	0.6648	56.7	0.4019
7	0.71	60	18.5	0.6551	59.2	0.4135
8	0.85	50	18.5	0.6343	61.8	0.3162
9	0.85	60	22.5	0.6167	48.0	0.3156
10	0.25	110	15.0	0.6922	75.8	0.5594
11	0.39	110	23.5	0.6768	65.6	0.4734
12	0.565	100	29.0	0.6593	57.4	0.4035
13	0.71	90	31.0	0.6407	53.3	0.3641
14	0.25	130	20.0	0.6845	66.9	0.4882
15	0.39	130	31.5	0.6625	56.7	0.4005

Viscometer constant = 0.010662

Surface tension data were tabulated for pure components in API Project 44 (1) and calculated for mixtures by Deam's (6) equation

$$\sigma_{mix} = \sum_i x_i \sigma_i + \sigma^E \qquad (5\text{-}1)$$

where excess surface tension, σ^E, is read from a graph with x_1, the mole fraction of the lighter component as the abscissa and σ^E as the ordinate, and lines of constant reduced temperature radiating from the origin.

Residual viscosity is independent of temperature and is a function of density only; it is widely used as a correlation technique. Therefore, this author reasoned that kinematic viscosity might be independent of density and would correlate better.

After drawing curves using both absolute and kinematic viscosity for the various correlations, the shapes were seen to be basically the same and neither would consistently fit the correlations better.

Absolute viscosities are reported in this thesis rather than kinematic. Generally, published viscosity data are absolute unless otherwise stated.

Bennett (2) tested the reproducibility of results from the apparatus and found they were within $\pm$ 25 per cent of literature data for n-nonane. The only difference in accuracy of data between this work and Bennett's is due to differences in technique.

CHAPTER VI

DISCUSSION OF CORRELATIONS

Bennett (2) showed that plots of the logarithm of surface tension as a function of reciprocal viscosity for mixtures yield straight parallel lines (Figure 10). He theorized that graphs using the same coordinates for other mixtures would be similar. However, he lacked sufficient data points over a wide enough composition range to prove this.

Definition of Error Reporting

Since the Bennett correlation did not work, others from the literature were used and modified to determine the one that would most faithfully reproduce experimental data. The accuracy is reported as average absolute and maximum positive and negative per cent difference between calculated and experimental points unless otherwise stated.

Per cent difference is defined as

$$\% \text{ diff} = \frac{\text{calculated viscosity} - \text{experimental viscosity}}{\text{experimental viscosity}} \tag{6-1}$$

The average absolute per cent difference is defined as

$$\text{ave abs } \% \text{ diff} = (1/n) \sum_{i}^{n} \left| \% \text{ diff}_i \right| \tag{6-2}$$

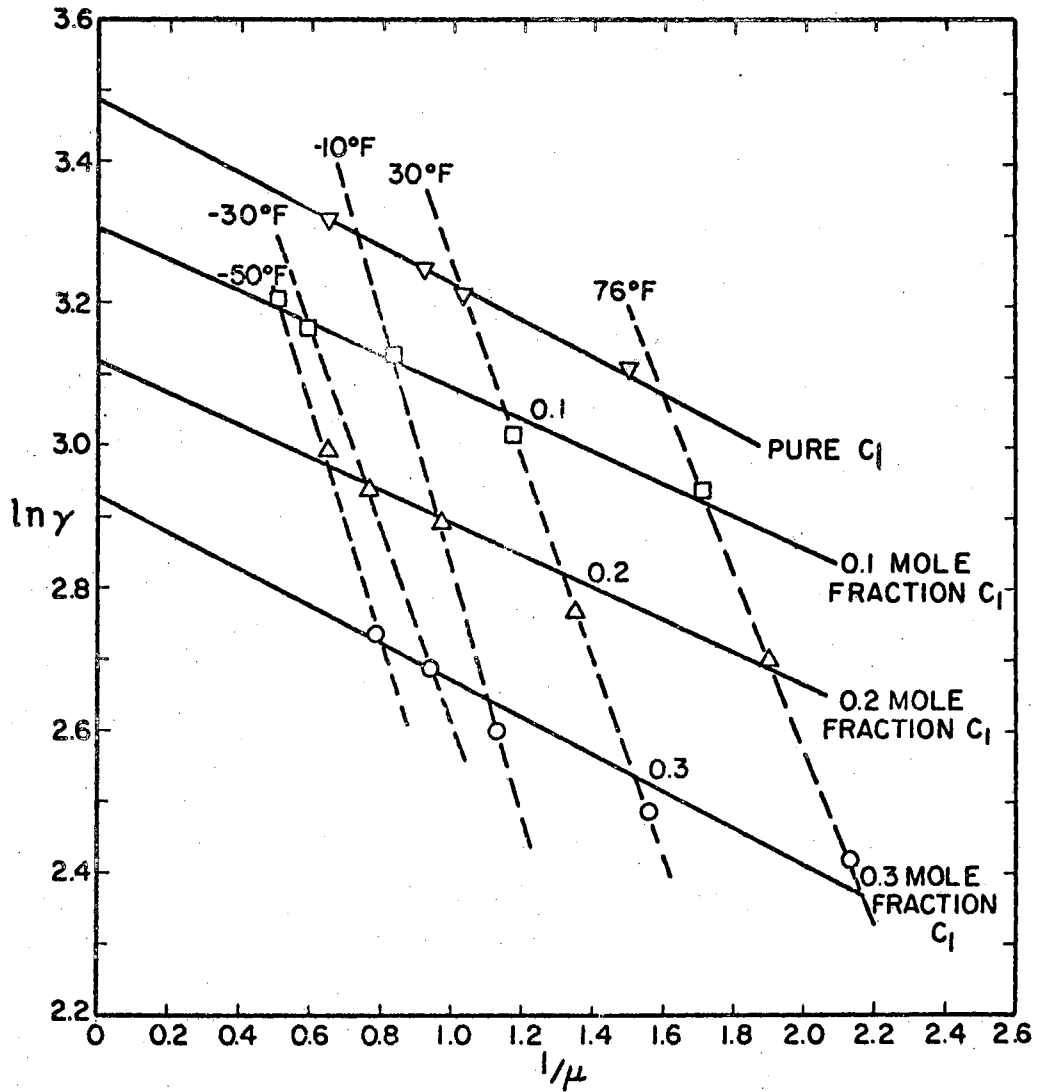A star (*) in the maximum positive per cent difference site shows

Figure 10. Bennett Correlation for Methane-n-Nonane

that all calculated points were less than experimental and only negative
values of per cent difference were calculated. The reverse is true for
a star (*) in the maximum negative per cent difference site.

Surface Tension-Viscosity

Using Bennett's coordinate system, the resultant graphs are indeed
parallel straight lines of constant composition and convergent straight
isotherms for methane-decane (Figure 11). The butane-decane plot
(Figure 12) is inconclusive because the points seem an extension of
the pure decane line. This method of correlating viscosity does not
work for these two systems since the graphs show that mixture viscosity
is not a simple function of the pure component viscosity. On Figure
11 the decane line should be positioned closest to the ten per cent
methane line, not the 70 per cent methane line. The butane-decane
system points were clustered together so that definite lines could not
be drawn with assurance. The hexadecane-tetradecane-hexane systems
were not correlated by this method as all points were along a single
isotherm.

Gas Mixture Viscosity Correlations

The equation using molecular weight by Herning and Zipperer (7),
Equation (2-24), was tested on the butane-decane system. The ratio of
experimental viscosity to calculated viscosity ranged from 1.76 to
2.94.

Buddenberg and Wilke (4) suggested using diffusivity and density
as variables in Equation (2-20). The average absolute and maximum
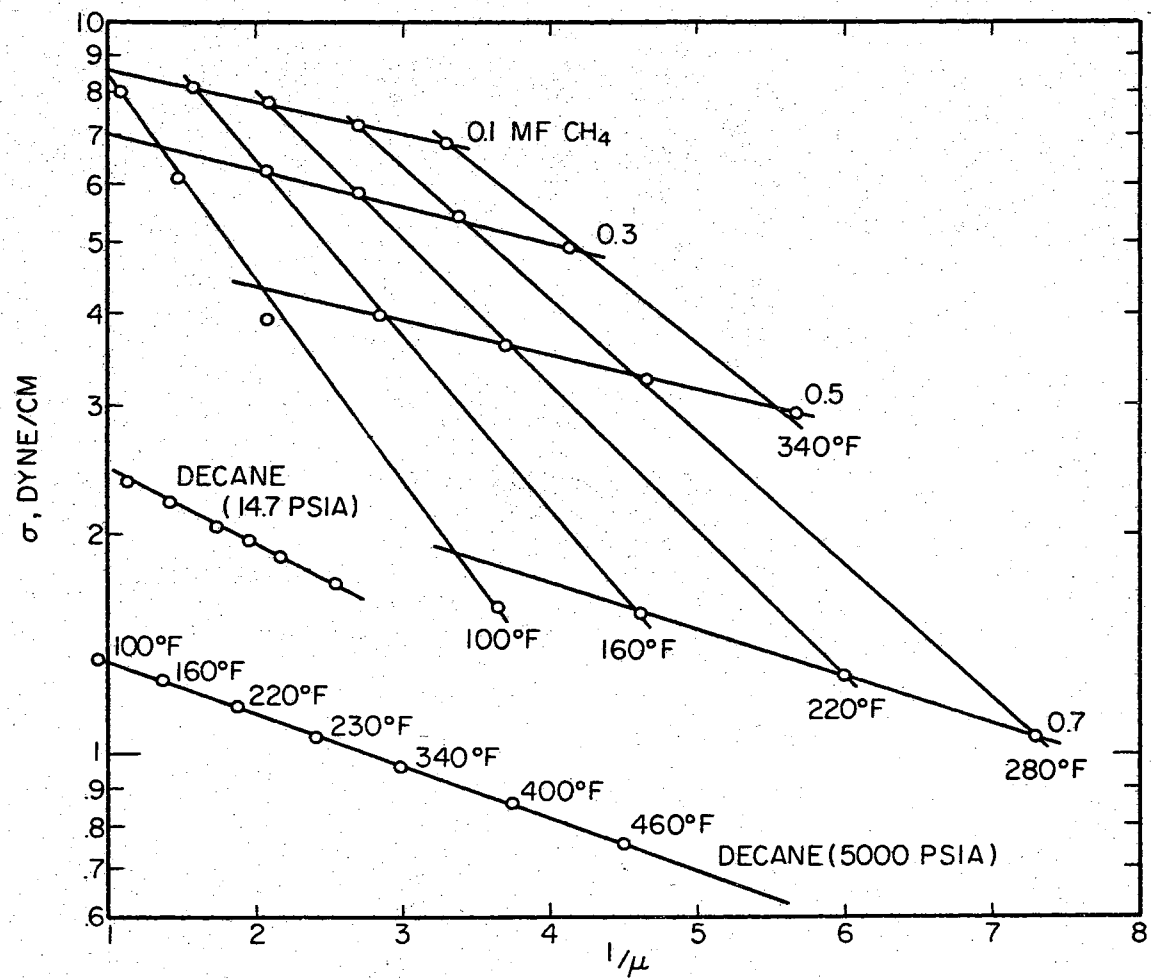positive and negative per cent differences for the butane-decane system

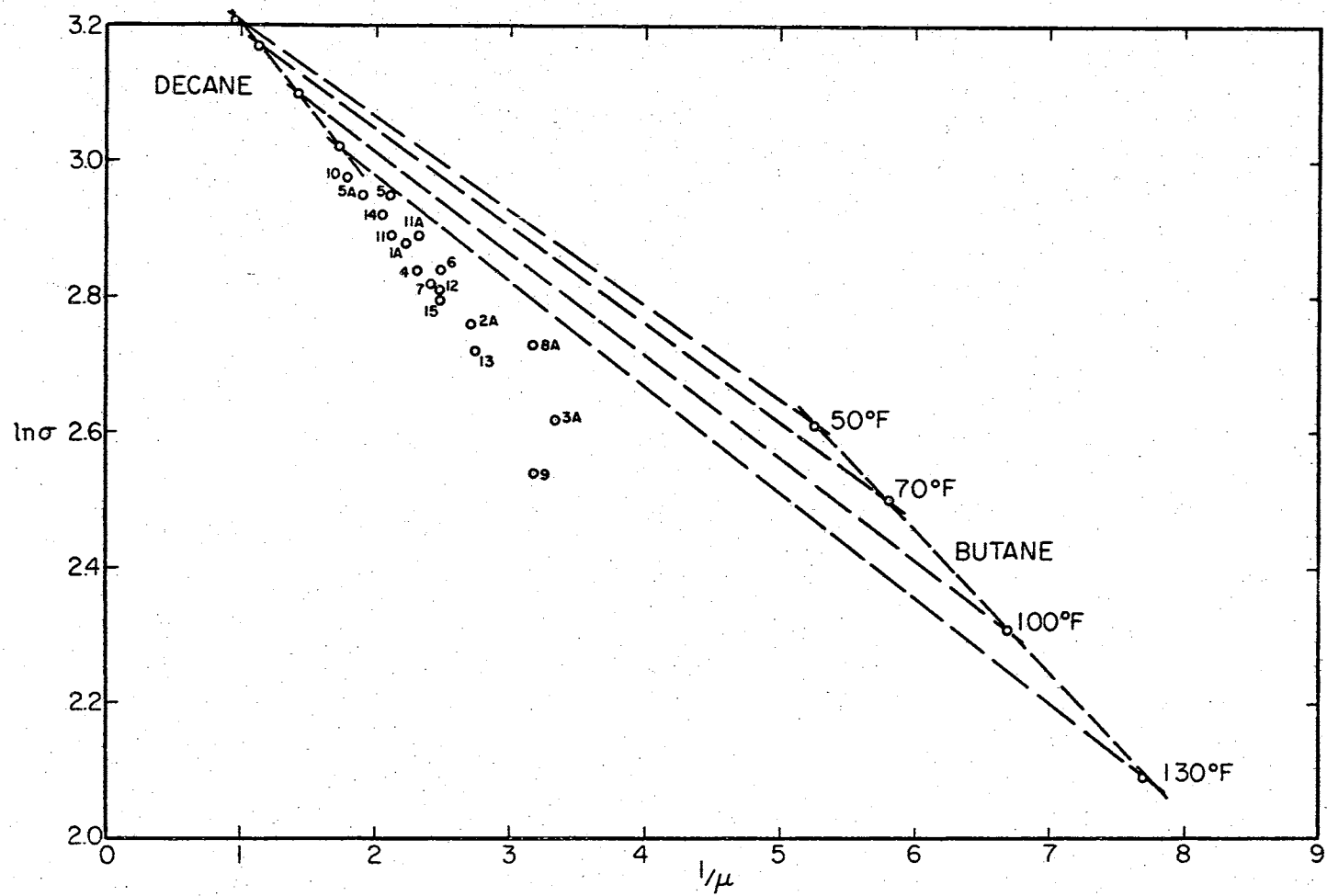Figure 11. Bennett Correlation for Methane-n-Decane

Figure 12. Bennett Correlation for n-Butane-n-Decane

were 68.3, 185.0, and -31.6 per cent, respectively.

Both of the above equations were for gas mixtures, but this author tested them for liquids.

Mixing-Rule Correlations

Using the two mixing-rule equation below, the errors were approximately the same. The Kendall and Monroe (21) equation, Equation (2-12), used viscosity to the one-third power and the average absolute and maximum positive and negative per cent differences were 16.6, 2.1, and -29.7 per cent, respectively, for the butane-decane system. Arrhenius, as reported by Gambill (12), used the weighted sum of logarithms of viscosity in Equation (1-3). The average absolute and maximum positive and negative per cent differences were 25.3, *, and -32.8 per cent for butane-decane, 19.8, *, and -24.6 per cent for hexane-hexadecane, 13.3, *, and -17.8 per cent for tetradecane-hexane, and 0.562, 1.41, and -0.306 per cent for hexadecane-tetradecane, respectively.

Grunberg-Nissan Correlation

Grunberg and Nissan (15) introduced an interaction parameter to the Arrhenius equation as derived earlier in Equations (2-13) through (2-22). This author tested Equation (2-13) on the four binary systems since the parameter seemed determinable a priori. Grunberg and Nissan were not explicit in their definition of b in Equation (2-15) and this author tried three variations of the Margules equation.

$$b = \ln \gamma_1 / x_2^2 \qquad (6\text{-}3)$$

$$b = x_1 \ln \gamma_1 / x_2^2 + x_2 \ln \gamma_2 / x_1^2 \qquad (6\text{-}4)$$

$$b = \ln \gamma_2 / x_1^2 \qquad (6\text{-}5)$$

There was not much difference in the accuracy using the above three definitions, as is shown in Table II.

Heric and Brewer (17) listed experimental values of the excess free energy of activation of flow, G^E, for the hexadecane-tetradecane-hexane systems. These data were used to evaluate the constants in the Wilson equation, Equation (5-1).

$$G^E/RT = -x_1 \ln(1-A_{21}x_2) - x_2 \ln(1-A_{12}x_1) \qquad (6\text{-}6)$$

where

$$A_{12} \neq A_{21}$$

Wilson's equation was rearranged and used to evaluate activity coefficients for Equations (6-3), (6-4), and (6-5).

$$\ln \gamma_1 = -\ln(1-A_{21}x_2) + x_2 \left[\frac{x_2 A_{12}}{1-A_{12}x_1} - \frac{x_1 A_{21}}{1-A_{21}x_2} \right] \qquad (6\text{-}7)$$

$$\ln \gamma_2 = -\ln(1-A_{12}x_1) - x_1 \left[\frac{x_2 A_{12}}{1-A_{12}x_1} - \frac{x_1 A_{21}}{1-A_{21}x_2} \right] \qquad (6\text{-}8)$$

According to Orye and Prausnitz (26), Wilson's equation calculates values of free energy of activation of flow nearer to experimental than the Van Laar equation, but there was no improvement in the accuracy of the correlation. Using the calculated parameter gave worse results than the Arrhenius equation (Table II). One way to improve the effect of the parameter is to use experimental viscosity in Equation (2-22),

TABLE II

SUMMARY OF GRUNBERG-NISSAN CORRELATION

$$\ln \mu_m = x_1 \ln \mu_1 + x_2 \ln \mu_2 + x_1 x_2 Cb$$

b is evaluated by these equations:

A $\quad b = \gamma_1 / x_2^2$

B $\quad b = x_1 \gamma_1 / x_2^2 + x_2 \gamma_2 / x_1^2$

C $\quad b = \gamma_2 / x_1^2$

γ_i is evaluated by the Van Laar Equation

System	A	B	C
C_4-C_{10}	34.6	32.6	29.0
	*	*	*
	-43.2	-41.4	-37.0
C_{16}-C_6	27.8	36.0	41.5
	*	*	*
	-34.6	-47.6	-51.9
C_{14}-C_6	20.6	27.4	30.6
	*	*	*
	-26.0	-34.7	-38.1
C_{16}-C_{14}	0.694	0.728	0.728
	1.45	1.45	1.45
	*	*	*

Top number is average absolute per cent difference;

middle number is maximum positive per cent difference;

bottom number is maximum negative per cent difference.

but then d falls into the classification of experimentally-determined parameters and loses its uniqueness.

Corresponding States Correlation

Preston, Chapman, and Prausnitz (29) used the corresponding states principle for their correlation of transport properties of cryogenic liquids, as derived earlier in Equations (2-4) through (2-11).

The interaction parameter η_{12} for butane-decane was determined by solving Equation (2-10) for η_{12},

$$\eta_{12} = \frac{1}{2\phi_1\phi_2} \left[\eta_m - \phi_1^2\eta_1 - \phi_2^2\eta_2 \right] \qquad (6-9)$$

substituting experimental data into the right side of Equation (6-9), and averaging η_{12}. Calculated viscosities were determined by Equation (2-10) using the average η_{12}. Values of the Lennard-Jones parameters were taken from Hirschfelder, Curtiss, and Bird (18), plotted as a function of molecular weight, and extrapolated to obtain values for decane. Then $\log_{10}\eta_*$ was calculated for both experimental and calculated values of η. Both sets of $\log_{10}\eta_*$ points were fitted to Equation (2-4) by least squares. The correlation coefficients for the experimental and calculated points were 0.812 and 0.928, respectively. The average absolute and maximum positive and negative per cent differences were 1.33, 2.83, and -2.02 per cent, respectively, meaning that the points fit the curve well, and there is very good agreement between the experimental and calculated values (Table III). Where values for all the parameters can be determined, this correlation is the best tested. However, the interaction parameter must be

TABLE III

SUMMARY OF PRESTON, CHAPMAN, AND PRAUSNITZ
CORRELATION FOR BUTANE-DECANE

Run No.	exp	calc	$1/T^*$	$\log_{10}\eta^*$ exp	$\log_{10}\eta^*$ calc	% diff
1	0.4515	0.4522	0.765	2.8989	2.8896	0.023
2	0.3695	0.3561	0.842	2.8119	2.7959	-0.570
3	-.2993	0.2640	0.887	2.7204	2.6659	-2.005
4	0.4336	0.3884	0.857	2.8814	2.8335	-1.660
5	0.4744	0.5356	0.655	2.9204	2.9731	1.805
6	0.4019	0.4331	0.745	2.8484	2.8809	1.142
7	0.4135	0.3742	0.869	2.8608	2.8174	-1.516
8	0.3162	0.2870	0.931	2.7442	2.7022	-1.531
9	0.3156	0.2778	0.915	2.7434	2.6880	-2.021
10	0.5594	0.5601	0.562	2.9920	2.9926	0.020
11	0.4734	0.4979	0.634	2.9195	2.9414	0.751
12	0.4035	0.4224	0.734	2.8501	2.8700	0.699
13	0.3641	0.3436	0.820	2.8055	2.7803	-0.897
14	0.4882	0.5909	0.542	2.9329	3.0158	2.827
15	0.4005	0.4698	0.610	2.8469	2.9162	2.435

Average absolute % difference 1.327

determined, either using a mixture data point or by devising a technique to predict it.

Free Energy Correlation

Gambill (12) stated his investigation showed that an interaction parameter added to the Arrhenius equation was proportional to exponential reciprocal temperature and to the excess free energy. This author took Gambill's suggestion and adapted the Arrhenius equation by adding an interaction parameter which was an empirical function of temperature and/or free energy. The equations he used were

$$\ln \mu_m = x_1 \ln \mu_1 + x_2 \ln \mu_2 + AG^E \tag{6-10}$$

$$\ln \mu_m = x_1 \ln \mu_1 + x_2 \ln \mu_2 + \exp(B/T) \, G^E \tag{6-11}$$

$$\ln \mu_m = x_1 \ln \mu_1 + x_2 \ln \mu_2 + \exp(C/T) \tag{6-12}$$

where A, B, and C are experimentally determined constants.

These equations were tested using experimental free energy and free energy calculated by the Wilson and Van Laar equations for the hexadecane-tetradecane-hexane systems and by the Van Laar equation for the butane-decane system. The average absolute and maximum positive and negative per cent differences are tabulated for the various cases of this correlation (Table IV - A, B, C).

Reduced Viscosity Correlation

Stiel (36) presented plots of reduced viscosity as a function of acentric factor and reduced temperature, where reduced viscosity is defined as

TABLE IV A

SUMMARY OF THE PROPOSED CORRELATION

$$\ln \mu_m = x_1 \ln \mu_1 + x_2 \ln \mu_2 + AG^E$$

METHOD OF FREE ENERGY CALCULATION

System	Experimental	Wilson Equation	Van Laar Equation
$C_4\text{-}C_{10}$			4.26
			13.9
			- 9.33
$C_{16}\text{-}C_6$	0.163	0.693	1.43
	0.275	1.66	2.96
	-0.268	-1.08	-2.07
$C_{14}\text{-}C_6$	0.123	0.372	0.836
	0.451	1.22	1.05
	-0.130	-0.596	-1.72
$C_{16}\text{-}C_{14}$	0.323	1.30	1.35
	0.787	1.20	1.20
	-0.136	-2.11	-2.21

Top number is average absolute per cent difference;

middle number is maximum positive per cent difference;

bottom number is maximum negative per cent difference.

TABLE IV B

SUMMARY OF THE PROPOSED CORRELATION

$$\ln \mu_m = x_1 \ln \mu_1 + x_2 \ln \mu_2 + e^{B/T} G^E$$

METHOD OF FREE ENERGY CALCULATION

System	Experimental	Wilson Equation	Van Laar Equation
C_4-C_{10}			8.06
			19.2
			-11.3
C_{16}-C_6	0.163	0.712	1.43
	0.274	1.63	2.85
	-0.266	-1.11	-2.15
C_{14}-C_6	0.123	0.377	0.855
	0.449	0.21	1.00
	-0.131	-0.608	-1.79
C_{16}-C_{14}	0.103	0.744	0.830
	0.199	1.33	1.49
	-0.00745	-0.946	*

TABLE IV C

SUMMARY OF THE PROPOSED CORRELATION

$$\ln\mu_m = x_1\ln\mu_1 + x_2\ln\mu_2 + e^{C/T}$$

METHOD OF FREE ENERGY CALCULATION

System	Experimental	Wilson Equation	Van Laar Equation
C_4-C_{10}			5.73
			13.4
			-10.6
C_{16}-C_6	4.51	4.51	4.51
	8.00	8.00	8.00
	-6.55	-6.55	-6.55
C_{14}-C_6	4.02	4.02	4.02
	8.71	8.71	8.71
	-6.00	-6.00	-6.00
C_{16}-C_{14}	0.748	0.748	0.748
	1.81	1.81	1.81
	*	*	*

$$\phi = T_c^{1/6} / (M^{1/2} P_c^{2/3}) \qquad\qquad (6\text{-}13)$$

Each plot suggested reduced viscosity was a function of the independent variable.

The acentric factor graph showed where the viscosity of each paraffin at a reduced temperature of 0.7 would lie on this coordinate system. This author reasoned that acentric factor of a mixture is a function of composition only, so paraffin mixture curves should have the same general shape as the pure component. For methane-decane (Figure 13), the isotherms are convergent curved lines, as are the lines of constant reduced temperature. The butane-decane chart (Figure 14) shows parallel isotherms. An equation was not devised to represent this coordinate system.

For the nitrogen-ethylene system, Stiel (36) plots reduced gaseous viscosity, $\mu * \phi$, where $\mu *$ is gas viscosity and ϕ is defined by Equation (6-13), as a function of reduced temperature. This gave a single line for the various compositions of nitrogen-ethylene. For methane-decane (Figure 15) the isotherms converged into the 70 per cent methane composition line to give a triangular-shaped graph. The butane-decane data (Figure 16) were not over a sufficiently broad temperature range to get this triangular curve. No equation was used to correlate this system.
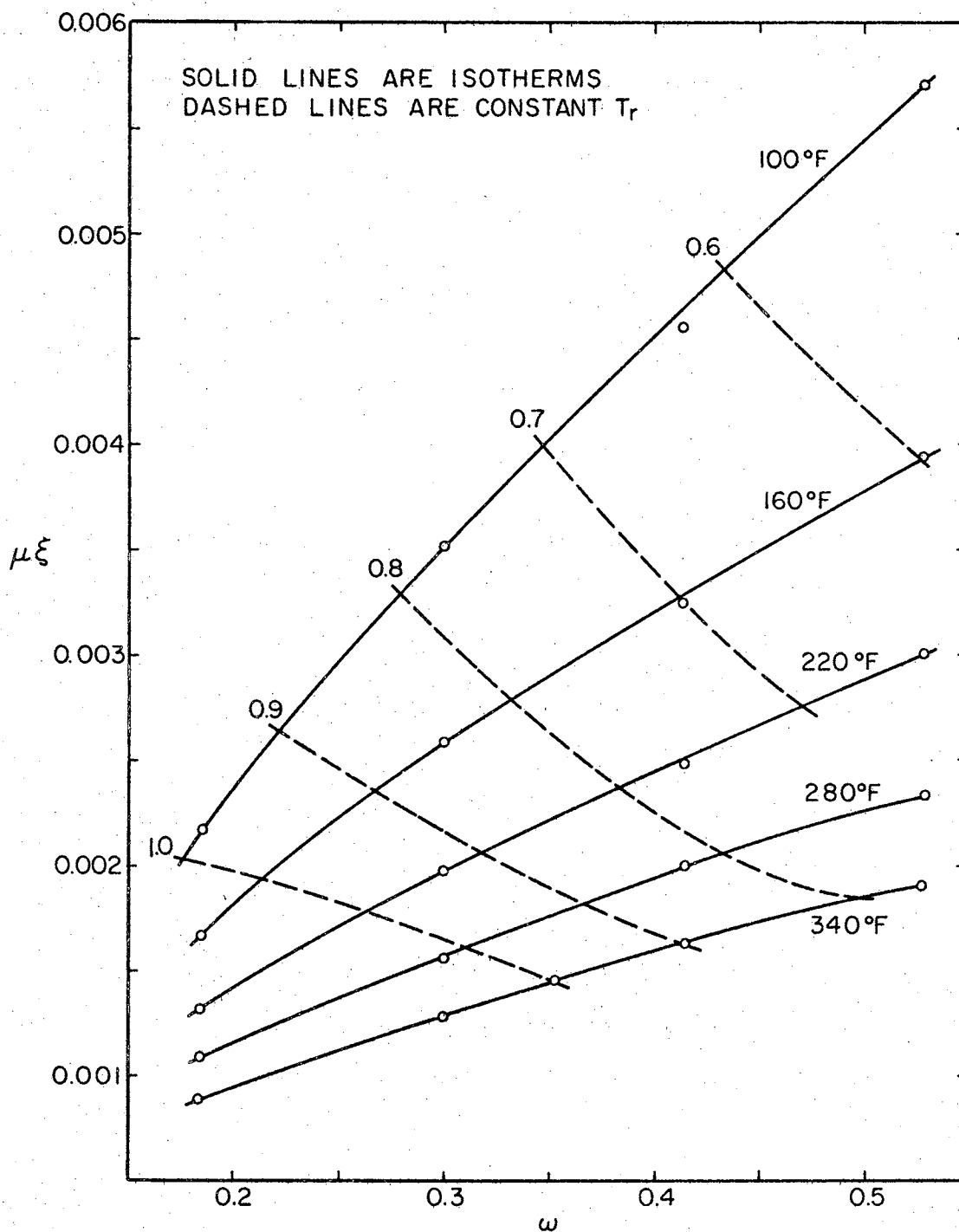
Figure 13. Stiel Acentric Factor Correlation for Methane-n-Decane
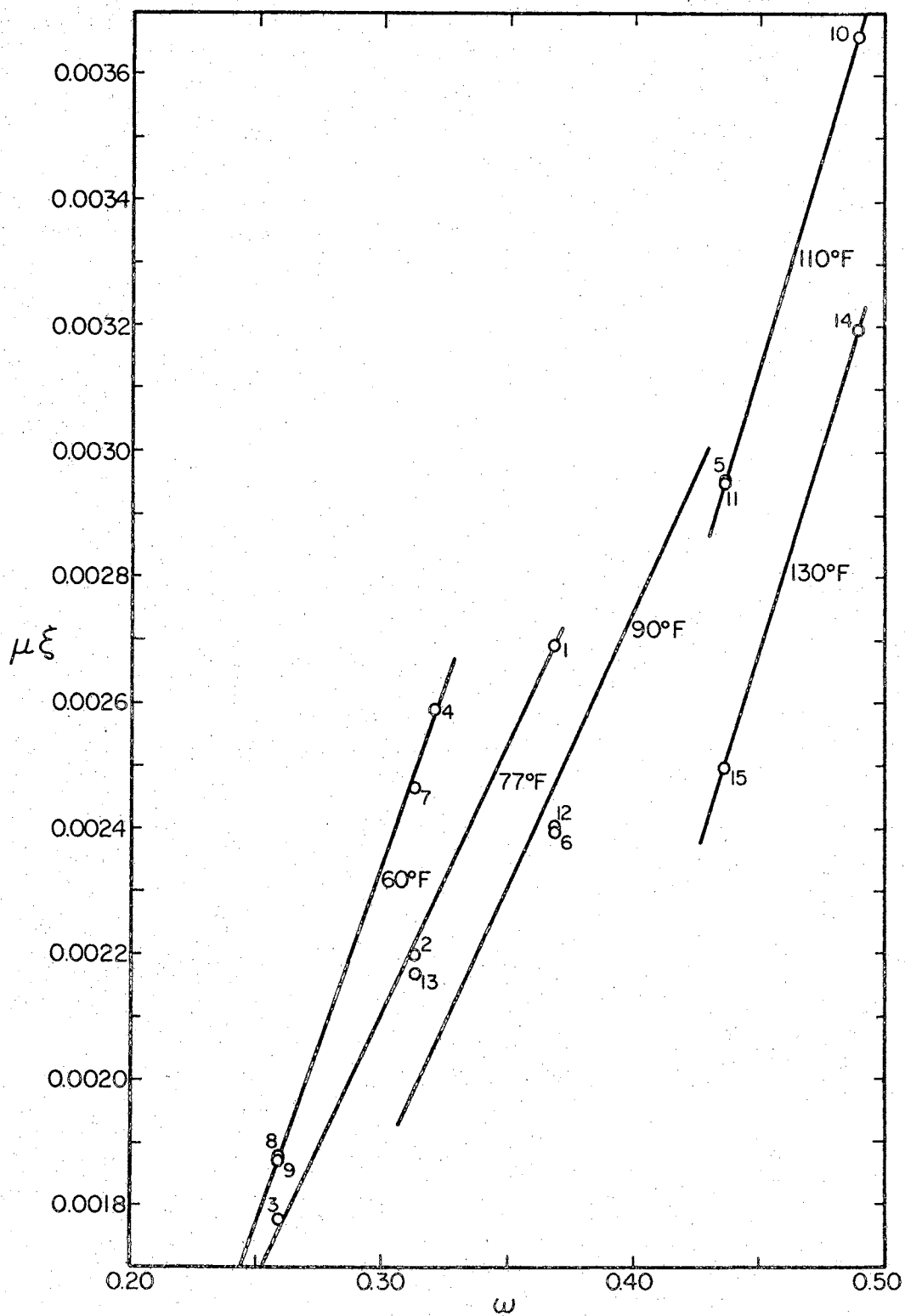
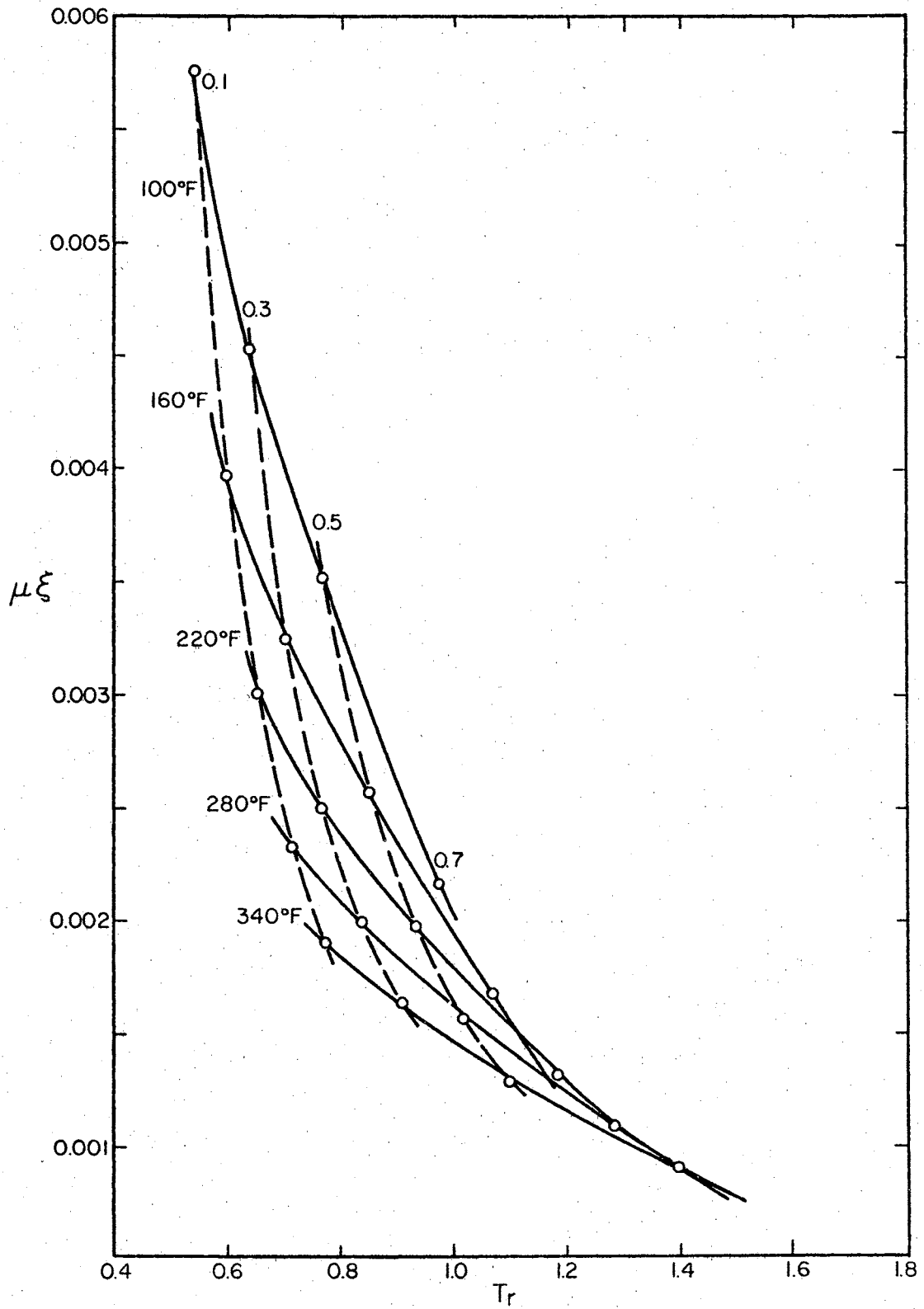Figure 14. Stiel Acentric Factor Correlation for n-Butane-n-Decane

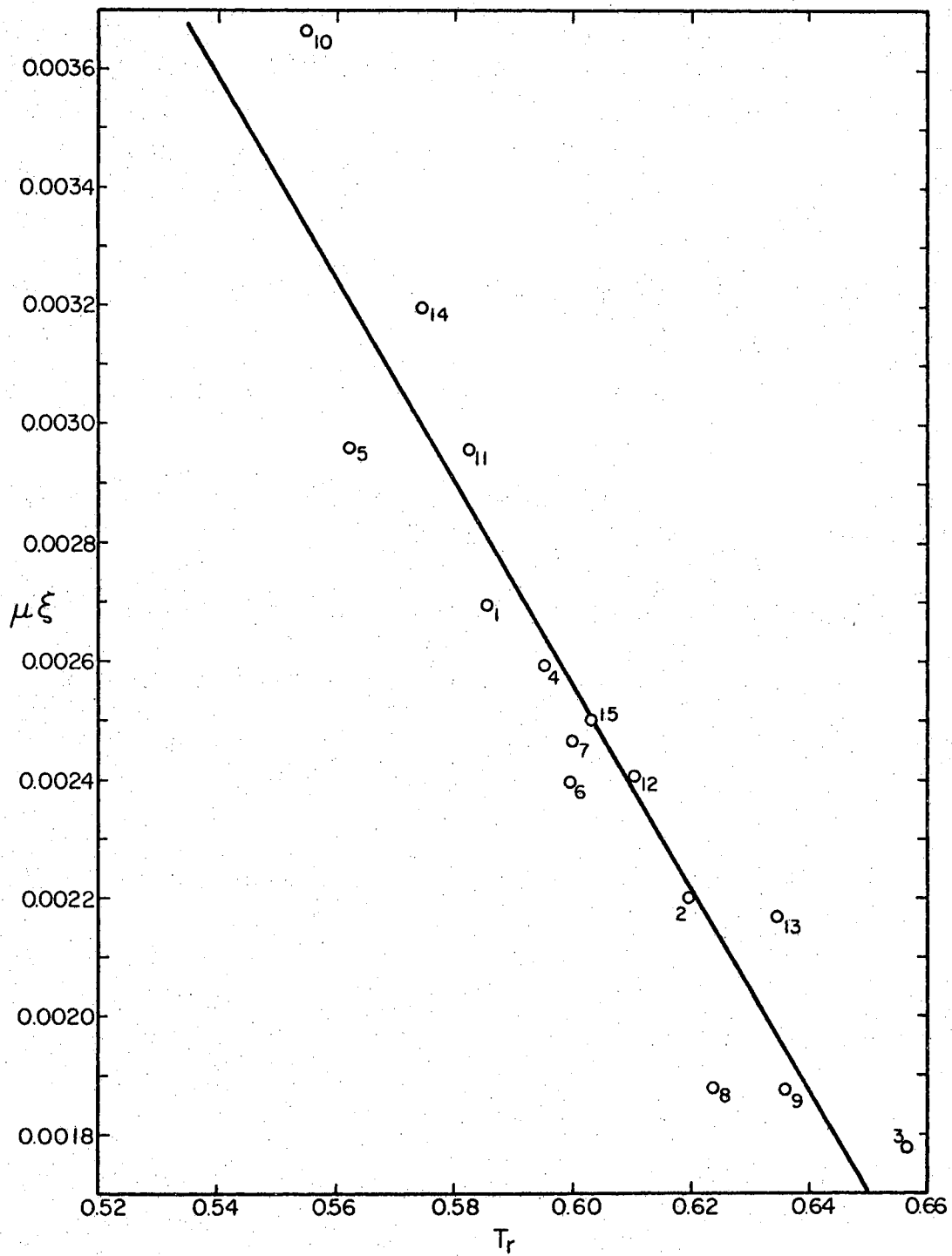Figure 15. Stiel Reduced Temperature Correlation for Methane-n-Decane

Figure 16. Stiel Reduced Temperature Correlation for n-Butane-n-Decane

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

The correlations studied were broken down into three basic types - graphical, equations without experimentally determined parameters, and equations with experimentally determined parameters. This author set as the requirement for a good correlation the ability to predict mixture viscosities within ten per cent of experimental.

Bennett's graphical technique (2) was found invalid for the systems tested. Stiel's coordinates (36) may work for some mixtures, but these results were inconclusive.

The equations of Herning and Zipperer (7), Equation (2-24), Buddenberg and Wilke (4), Equation (2-23), Kendall and Monroe (21), Equation (2-12), and Arrhenius (12), Equation (1-3), did not meet this requirement. The equation by Grunberg and Nissan (15), Equation (2-13), and adapted by this author also did not meet the ten per cent requirement. However, Equation (2-13) may be evaluated by other means to reduce the error. None of the above equations had an experimentally determined parameter.

The two types of equations that accurately predicted viscosity data had experimentally determined interaction parameters.

The corresponding states technique of Preston, Chapman, and Prausnitz (29) predicted point values of viscosity very well and also reduced the data to a simple function of reduced temperature.

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However, the procedure is quite involved and requires the use of Lennard-Jones parameters and critical volumes of pure components.

This author proposed three equations using combinations of an experimentally determined constant, temperature, and excess free energy of mixing as parameters. They are Equations (6-10), (6-11), and (6-12). The main disadvantage of this type of correlation is that it requires values of the excess free energy of mixing, G^E. This G^E may be evaluated by the Wilson or Van Laar equations or experimentally. Both equations have constants to determine, by curve-fitting experimental data or some other means. Edmister (11) shows how to calculate the Van Laar constants using critical pressure and temperature. But the Van Laar equation is the least accurate, especially with constants determined in this manner. In spite of these difficulties, this correlation predicts mixture viscosity very well.

Both techniques are straight forward and can be directly programmed for computer usage or could be used for hand calculations. There are no trial-and-error steps or logic functions required in either process.

Recommendations

Persons continuing this work are recommended to do the following:

1. Evaluate the interaction parameter of Preston et al. (29) /Equation (2-10)/ for other mixtures and correlate it.

2. Apply the proposed correlation /Equations (6-10), (6-11), and (6-12)/ to more systems.

3. Evaluate the Grunberg-Nissan (15) parameter /Equation 2-13)/ experimentally and correlate it.

4. Adapt the apparatus to time runs electronically and invent a technique to take samples of the fluid in the reservoir to analyze chromatographically. Install a device to read pressure inside the cylinder.

5. Test Stiel's graphical coordinates (36) on other mixtures.

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NOMENCLATURE

ENGLISH LETTERS

A, B, C, ... Empirical constants

G^E Excess free energy of activation of flow

k Boltzmann's constant

M Molecular weight

P_c Critical pressure

r_o Intermolecular distance at minimum energy

T Absolute temperature

T_c Critical temperature

T_r Reduced temperature, T/T_c

T^* Reduced temperature, kT/ϵ

t Temperature, ^{o}F or ^{o}C

V Volume

V_c Critical volume

x_i Mole fraction

Z_c Critical compressibility factor

GREEK LETTERS

γ Activity coefficient

ϵ Lennard-Jones energy parameter

η Absolute viscosity, cp

η^* Reduced viscosity according to Preston, et al., Equation (   )

η_{ij} Viscosity interaction parameter

ν Kinematic viscosity, cs

ξ Viscosity parameter, $T_c^{1/6}/(M^{1/2}P_c^{2/3})$

ρ Density

σ Surface tension, dyne/cm

τ Time, sec

ϕ_i Volume fraction, $x_i V_{ci}/\sum_i x_i V_{ci}$

μ Liquid viscosity, cp

μ^* Gas viscosity, μp

ω Acentric factor

VITA ⅔

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