THE VISCOSITIES FOR HYDROCARBON SYSTEMS

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THE EFFECT OF COMPOSITION AND PRESSURE UPON THE VISCOSITY FOR A THREE COMPONENT HYDROCARBON SYSTEM

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I NTRODUCTION

As a part of a coordinated research program being carried out by the American Petroleum Institute Project No. 37, this study of the effect of pressure and composition upon the viscosity of the methane, propane, crystal oil system was made in an effort to correlate further the physical behavior of hydrocarbons. Since the study of a three component system over the whole range of compositions, temperatures, and pressures is a large task, this research was limited to a temperature of 100° F, and to that region of compositions bounded by a maximum of' 5 mass per cent methane and 20 mass per cent propane. The viscosities were measured in the pressure range from below bubble point to 3000 pounds per square inch, which was the maximum pressure allowed by the design of the apparatus.

The work reported in this thesis consists of a de scription of the viscometer, of tabulated values of viscosity for the experimental compositions investigated and of a graphical presentation of viscosity and phase

equilibrium data derived from the experimental values.

MATERIALS USED

The crystal oil used was a highly-refined waterwhite paraffin base oil produced from Pennsylvania crude; its constituents had a narrow range of high molecular weights and consequently the oil was of low volatility, and of moderately high viscosity. Its molecular weight was determined by the freezing-point method in benzene and found to be approximately 342. Its density at 100 ^TF was 0.8244 grams per cc. The sample was obtained through the courtesy of the Union Oil Company of California.

The propane used was obtained from the Philgas Company, of Bartlesville, Oklahoma who reported the special fractionation analysis 100.00% propane. Investigation showed the bubble-point and dew-point varied by less than 0.5 pounds per square inch, thus substantiating the Philgas Company's analysis.

The methane used was prepared from natural gas in equipment already developed by the Project 37 for removal of the higher molecular weight hydrocarbons by compression, cooling, and subsequent liquefaction of the undesirable components. Further treatment of the methane with activated charcoal served to remove small amounts of ethane and higher hydrocarbons to the extent that less than 0.02 per cent remained in the methane gas. Partial solidification at liquid air temperatures and 1.05 pound per square inch pressure served to remove all but a trace of the nitrogen and similar gases.

DESCRIPTION OF THE APPARATUS

The instrument used was the rolling ball viscometer adapted by Sage (1) from the earlier forms used by Flowers (2) and Hersey (3) . In principle it consists of a ball moving down (by a combination of rolling and sliding, whence the name "rolling ball") an inclined, liquidfilled tube for a fixed distance. The annular clearance between the ball and the walls of the tube is on the order of a .01 inch so that viscous flow of the liquid past the ball is maintained over the major portion of the viscosity range. Thus, for a given ball, the value of $t(e-e)^{\frac{1}{n}}$ is a linear function of absolute viscosity of the liquid. However for low viscosities, as is shown by a sample calibration curve, the flow through the annular space becomes turbulent, and the relationship between viscosity and the parameter $t(e_a - e)$ is no

> l Notation: $t = roll$ time, seconds ρ_{\circ} = density of ball grams/cc.
 ρ = density of liquid grams/cc.

longer linear. Another factor which enters into this deviation from linearity is the acceleration during starting, which is, however, negligible for all except the shortest of roll times (15 seconds) as may be judged from the fact that the complete roll time of the ball down the clean air-filled tube is only 1.3 seconds.

A schematic diagram of the instrument developed for the measurement of viscosities in the condensed region as well as for the two phase region is shown in Figure I. The liquid under test was circulated through the saturation cell Δ , to the variable volume cell \underline{B} thence up the roll tube of the viscometer proper, and returned to the saturation cell to the cam pump. A vane agitator was provided in the upper part of the saturation cell to assist rapid attainment of phase equilibrium. The system was so arranged that any entrapped gas in the roll tube was swept out by the circulating liquid and into the gas space in the top of the saturation cell. The total volume of the closed circulating system could be varied about twenty per cent at the will of the operator by admission to or release of mercury from the bottom of the variable volume cell; permitting the measurement of viscosities in the condensed region. The upper pressure limit was set at 3000 pounds per

square inch by the design of the instrument.

EXPERI MENTAL METHOD

In operation, the entire system was filled with a weighed oil sample, which after attainment of thermal equilibrium, (requiring l to 2 hours) was circulated through the roll tube, forcing the ball to the top, above the outlet tube, and removing any gas bubbles from the viscometer tube. Circulation was then stopped. the ball allowed to roll part of the way down the tube, and then the upper contact was screwed down a definite small distance. Starting the circulation again pumped the ball up the tube and wedged it against the upper contact $pin.$ ¹ Circulation was stopped, the valve at the lower end of the roll tube closed, and after a short wait to allow the turbulent currents to cease the upper contact was lifted, starting the ball down the tube and actuating an electric chronograph. The ball, on striking the lower contact, again actuated the chronograph and the roll time was thus recorded. The valve at the bottom of the roll tube was then opened, circulation started again and the measurement

 $\frac{1}{\text{This procedure gave quite reproducible results}}$ even though the upper contact may be reset a dozen times during the course of a run.

repeated until a constant value was obtained. The pressure on the system was then increased by admission of mercury at a high pressure to the bottom of the variable volume cell, equilibrium reestablished by circulation, and a viscosity measurement then taken at the higher pressure, which was maintained eonstant by the use of fluid pressure scales. When the pressure limit had been reached, the pressure was dropped to below bubble-point by release of mercury, more gas was then forced in, and the whole series of measurements repeated on the liquid for both the two phase and the condensed region for the new composition. It was the usual experience to obtain one or two values for pressures below bubble-point, one value at bubblepoint, and then values for the condensed region at gauge pressures for even 500 pound intervals to 3000 pounds per square inch.

MEASUREMENTS

The pressure on the system was measured by means of a fluid pressure scale connected to the mercury in the bottom of the variable volume cell through a mercury trap. the transmitting fluid being transformer oil. The fluid pressure scales used were sensitive to 0.1 pound up to 300 pounds and to 1. pound up to 3000 pounds.

The crystal oil sample was added from a glass weighing flask. The propane was weighed in from a small steel bomb. All weighings were by difference, and were accurate to 5 mg., representing an accuracy better than .1% for the smallest addition made. The methane was added under pressure from a calibrated. reservoir, with an accuracy of .3% by weight.

The temperature of the viscometer was held at the desired value by means of an oil bath and an electric heater controlled by a mercury regulator, which maintained the temperature within a .04 $^{\circ}$ F. of the fixed temperature. The maximum observed temperature variation from point to point in the bath was less than 0.1° F. Temperatures were measured with a mercury-inglass themometer with graduations to 0.1° C and having a Bureau of Standards calibration. Exposed stem correction for the temperature of 100° F (or 37.76°C) amounted to only 0.07[°]F.

Time was measured with an electric chronograph having an electromagnet actuated recording pen, and a drum driven by a small synchronous motor which was, of course, subject to minor variations in the line frequency amounting to not more than 0.1%. The design was such that one inch of tracing represented one second, thus allowing the estimation of the elapsed time to 0.01

·second.

CALIBRATION

The calibration of the viscometer was carried out with the liquids of known viscosity by following the general procedure outlined above, with the exception of the gas addition and attending manipulations. The ball was one which had been previously used, but the calibration was checked at six points and at two temperatures with two kinds of crystal oil and a kerosene. The viscosity of one oil, (a western oil having a high naphthenic content and hereafter referred to as crystal oil B) was known from previous work (4) , while the viscosity of the previously described oil (an eastern paraffin base oil, and hereafter referred to as crystal oil C) was determined at 100[°] and 160[°]F with a previously calibrated Pyrex Ostwald viscometer. The viscosity of the kerosene was similarly determined in a quartz Ostwald instrument. These points, together with the points determined earlier were used in drawing the calibration curve shown in Figure II. For the rolling ball viscometer the viscosity is proportional to the roll time and to that component of gravity determined by ·the angle of the roll tube and the difference in density between the ball and the liquid. The angle of the roll tube is constant, hence so long as

Calibration Curve

the liquid flows past the ball is viscous, the parameter of roll-time multiplied by the difference in densities of ball and liquid is a linear function of viscosity. Examination of the calibration curve indicated substantial linearity for the range 30 to 500 millipoises, with some indication of turbulent flow for viscosities of less than 30 millipoises.

The single ball used was sufficient to cover the full range involved, so no further calibrations were necessary, except as a check upon the accuracy of the calibration, for the work of Sage (1) indicated that any change in the surface condition of either ball or roll tube would cause large errors in the results. The ball used was precision ground from stainless iron (density 7.675) to within .0001 inch of spherical, and extreme care was observed in handling the ball to assure maintenance of an accurate calibration. The roll tube was of similar material and machined with equal paycision. Previous work of Sage (1) indicated that any effect of pressure on the calibration was negligible. Similarly, the effect of temperature on the calibration was found to be negligible.

CALCULATIONS

The calculations involved were simple. The liquid

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density for a given solution was calculated from the laws of perfect solutions, and the estimated compressability of the liquid and the value of the parameter $t(e_{s}-e)$ found from the corresponding roll time, t_{*} The viscosity was then read from the calibration curve and recorded as rough data. The rough values were plotted on a scale large enough to give readings of comparable accuracy with the experimental work $(0.5%)$, the best fitting curves drawn through the points and the smoothed values of viscosity read from the curve thus drawn. The excellent agreement of the values may be seen from Figures III, V, VI, and VII, in which the actual experimental points are shown for the different compositions. The compositions were calculated both on the basis of weight per cent and mol per cent, using an average value of molecular weight of 342 for crystal oil C. The viscosities for the experimentally studied compositions are tabulated and shown in Appendix A. The arrangement is in the order of increasing mass ratio of propane to crystal oil.

At this point it is perhaps advisable to explain the "mass ratios" as used in this thesis. As is well known, to represent in full detail a given variable as a function of composition and an independent variable (pressure) for a three component system would require

The Viscosity of Crystal Oil as a Function of

Pressure

The Increase in Viscosity of Crystal oil With Pressure Expressed as a Ratio of the Viscosity Under Pressure to that at its Vapor Pressure.

more than three dimensions. One possible solution is the tabulation of viscosity for each composition and pressure, such as has been done for the experimental compositions. The only other alternative for convenient presentation is to show one variable as a function of two others with the restriction that the ratio (either molal or weight) of two components must remain constant. For this work, the mass ratio of propane to crystal oil was chosen as the most convenient ratio to i hold constant, as it arose directly from the experimental procedure, in which the propane was added first **Processing Company's** to the crystal oil, thus establishing a fixed weight ratio of the two. All subsequent changes in composition for this particular ratio were made by addition of methane to the system. As the experimentally determined molecular weight of a hydrocarbon such as crystal oil is of doubtful significance, all subsequent data (unless specifically stated otherwise) are presented on a mass basis; thus per cent and mass ratio of propane to crystal oil will be used in referring to composition.

EXPERIMENTAL RESULTS

The effect of temperature and pressure on crystal oil C was first investigated, with the results shovm in

Figure III, in which the viscosity is shown as a function of pressure for temperature at 50° intervals from 100° to 220° F, inclusive. The effect of temperature on viscosity, is, as usual, much greater for the lower temperatures. The effect of pressure is most marked for 100° F, for which the viscosity at 3000 pounds absolute is 144% of that at approximately O pounds per square inch absolute. This percentage is progressively less for each succeeding higher temperature, amounting to only 132% at 220 $^{\circ}$ F. The ratio for each temperature as a function of pressure is shown in Figure IV. Entirely similar results to those shown in Figures III and IV were obtained for crystal oil B (4) , and for a kerosene, but no means of correlation is suggested by the data, except the possibility of an empirical relationship based on specific gravity, molecular weight, or some similar factor. However, the derivation of such and empirical formula would require far more data than was obtained in the study of these substances.

METHANE-CRYSTAL OIL SYSTEM

As a result of the work done on crystal oil C, the temperature of 100° F was chosen as having the most convenient range of vi scosity for the subsequent work on the two and three component systems. The first of the two

component systems studied was that of methane and crystal oil C. the experimental results of which are shown in Figure V. The pressure-viscosity curve for pure crystal oil is shown, as well as those for four compositions ranging from 0.584 to 4.00 mass per cent methane and to a maximum bubble point of 2290 pounds per square inch. The number of points in the two phase region was sufficient to permit the drawing of the two-phase curve, which is of the same nature as the saturation-pressure, viscosity curves previously reported by Sage and coworkers (4) . It should be noted that the curve is not a true bubble point curve, since for pressures much below bubble point the volume of the gas phase was an appreciable fraction of the whole. The effect of the relative volume of gas space on the liquid viscosity is difficult to estimate, for though some transference of the lighter components to the gas phase takes place, particularly at the higher pressures, the necessary information is lacking which would permit a quantitative calculation. T.t. is the belief of the author that such a transference of the lighter components to the gas phase would tend to increase the liquid viscosity. Critical examination of the experimental results permits the conclusion that for bubble point pressures up to 2500 pounds per square inch and a gas volume of not more than 15% of the whole, such

Viscosities at Bubble-Point and in the condensed Region for the Methane Crystal 011

System

saturation-pressure, viscosity curves as obtained with this viscometer in the two phase region represent substantially the bubble-point viscosity curves.

In the condensed region, it will be noted in Figure V, the pressure viscosity curve for the lowest mass per cent methane is of similar shape as that for pure crystal oil, showing a slight upward curvature and indicating as for crystal oil, an increasing pressure coefficient of viscosity with pressure. For the higher methane concentrations, the effect of pressure on the absolute viscosity is less. However, the per cent increase is still large as may be seen from Figure VIII, in which the ratio of viscosity for the condensed region to that for bubble point is plotted as a function of the pressure increment above bubble point. Examination of the figure indicates, also, the much greater effect of methane at the lower concentrations. Further discussion of the effect of concentration on viscosity is given in a later section. in which an attempt is made to correlate the results of the experimental studies.

THE PROPANE-CRYSTAL OIL SYSTEM

The propane-crystal oil system was studied over

 1 Pressure coefficient of viscosity is defined as

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the bubble point pressure range from 20 to 130 pounds per square inch absolute, with a maximum concentration of approximately 17 per cent propane. The bubble point curve for this system, as shown in Figure VI, indicates a large change in viscosity with change in pressure, as might be expected from the large solubility of propane in the oil at 100°F. The experimental points for the two phase region all lie on a single curve which represents, within the limits of experimental accuracy, the bubble point viscosity.

The effect of pressure on the viscosity in the single phase region is best shown in Figure IX, in which the ratio of the viscosity for a mixture in the condensed region to that at its bubble point is plotted against the corresponding pressure increment above bubble point for the concentrations $1, 5,$ and $15%$ propane. The curves are in many respects similar to those for methane, except that the effect of propane is not as large as that of methane, when compared on a mass per cent basis. Further discussion is given in a later section.

THE METHANE, PROPANE, CRYSTAL OIL SYSTEM

This system was studied for compositions up to 17% propane and 4% methane, with propane to crystal oil ratios ranging from 0.018 to 0.213. A graphical presenta-

Viscosities at Bubble-Point and in the Condensed Region for the Propane, Crystal Oil

System

tion of the actual experimental results for the two ratios mentioned is given in Figure VII. As may be seen. the figure is in effect a combination of the two types represented in Figures V and VI for methane and propane respectively. For the family of curves having a propane to crystal oil ratio of 0.018, it will be seen that the effect of methane on the bubble point viscosity is still quite large, and the condensed region curves appear similar to those for methane-crystal oil alone, with the obvious exception that the 'bubble point viscosity for zero per cent methane is now the viscosity of the propane. cr ystal oil mixture.

Increasing the weight ratio of propane to crystal oil has the effect of shifting the initial viscosity down the propane bubble-point curve. The effect on the vis-,cos1 ty o.f adding methane is much less at the higher propane concentrations, as will be noted from the small change in viscosity (see Figure VII) upon addition of 4% methane to a solution having the high propane to crystal oil ratio of 0.213. The transference of some of the less volatile components to the gas phase undoubtedly takes place in the two phase region for the higher pressures. but as is explained in the section covering the methane, crystal oil system, the net effect on the viscosity is negligible. In an effort to correlate the effect of

Figure VII

Viscosities at Bubble-Point and in the Condensed Region for the Methane Propane, Crystal Oil System.

composition on bubble-point viscosity, graphical interpolation was used to obtain the family of curves presented in Figure *X,* in which the effect on the bubble point viscosity of the mass per cent methane in the solution *is* shown for even values of the propane to crystal oil ratio. An examination of the figure shows that a simple correlation of bubble point viscosity and mass composition is improbable.

In the condensed region, a similar correlation is out of the question, as is evident from a comparison of Figures VIII and IX, which give the viscosity ratio $\frac{1}{2}$ **//**_{bp} for fixed compositions as a function of the pressure increment above bubble point. A correlation would not be expected, since the total pressures for these two cases are widely different for the same value of pressure increment. As shown in the upper curve of Figure IV, the viscosity coefficient of pressure, $(d\eta/dp)$, increases with pressure for the crystal oil. Secondly, the effect of methane and propane and the η / n_{bn} ratio cannot be compared satisfactorily by a diagram similar to Figure VIII, since the pressure limitations of the viscometer precluded the necessary measurements on the methane, crystal oil system.

The bubble-point viscosity of the methane. propane, crystal oil system as related to the per cent methane.

Pigure VIII

The Increase in Viscosity with Pressure for Mixtures of Methane and Crystal Oil in the Condensed Region. The ordinate represents the ratio of the viscosity under pressure. to that at the bubble point of the mixture. The abcissae represents the pressure increment above the bubble point of the mixture.

The Increase in Viscosity with Pressure for Mixtures of Propane and Crystal Oil in the Gondensed Region. The ordinate represents the ratio of the viscosity under pressure to that at the bubble point of the mixture. The abcissae represents the pressure increment above the bubble point of the mixture.

Mgure IX

A POSS!BLE MEANS OF CORRELATION

Previous discussion and the figures presented therewith have shown the difficulties of correlation of viscosity as a function of mass composition. Therefore a comparison on a molal composition basis was attempted. The results are shown in Figures *XI, XII,* and XIII. In Figure XI, the bubble point viscosity is plotted as a function of the mol per cent crystal oil for the methane, crystal oil system. Viscosities at constant pressure in the condensed region are shown for 1000 and 2500 pounds per square inch. It is noted that the constant pressure lines terminate on the bubble point line at their respective bubble point compositions.

In Figure VII a similar plot is shown for the propane, crystal oil system. At once the similarity of the bubble-point viscosity curves for the two systems is evident, although the constant pressure lines for the condensed region in the case of propane do not intersect the bubble point curve. It is seen, however, that the bubble point viscosity of each two component system is practically the same function of the mol per cent of crystal oil $C¹$ This might be expected, since each

¹ This is not true for the systems methane, crystal oil *B*, and propane, crystal oil *B*, as is shown by the work of Sage (4), in which marked difference of molal effect on viscosity is noted. However, crystal oil B is from a western stock and is of high naphthenic content, and therefore is not a member of the paraffin series.

component is a member of the paraffin series; and methane and propane in solution are reasonably similar in properties.

For the three component system, methane, propane, erystal oil C, the bubble-point viscosity curve was drawn as shown in Figure XIII, based on the data for all the systems studied. Each system is differentiated by a particular notation and it may be seen that all the points lie close to the single curve. Some random scattering of points may be observed, attributable to errors in computation of molal composition on the basis *j* of an average molecular weight for the crystal oil.

Therefore, the conclusion is drawn that the bubblepoint viscosity for this system is a definite function of the mol fraction of crystal oil, irrespective of the proportions of the other two components. However, the unique relationship of the components of this system must be kept in mind in the extension of the foregoing conclusion to systems other than those presented in this thesis. That is, each of the components in the systems studied is a member of the homologous paraffin series; two are of low molecular weight, of high volatility, and in solution have reasonably similar properties; the third

¹The crystal oil C is from Pennsylvania crude, highly refined, and therefore largely a pure paraffin oil.

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Viscosities at Bubble - Point and in the Condensed Region for the Methane, Crystal 011 System as a Function of the Mol Fer Cent Crystal 011.

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Viscosities at Bubble-Point and in the Condensed Region for the Propane, Crystal Oil System as a Punction of the Mol Per Cent Crystal Oil.

Figure XII

Pigure XIII

Viscosities at Bubble-Foint and in the Condensed Region for the Nethene, Propane, Crystal 011 System as a Function of the Mol Per Cent Crystal Oil.

is of high molecular weight and low volatility.

Therefore, for complex hydrocarbon systems of the same nature as those here reported it should be possible to predict the bubble-point viscosity of the system with fair accuracy with data obtained from the study of a representative two component system, i.e., a viscosity study for a system constituted of the heavy component and one light component. For example, it is possible to predict with reasonable accuracy the bubble-point viscosity of the methane, propane, crystal oil system from data obtained in the study of the propane, crystal oil system. Furthermore the bubble-point viscosity curve for such a two component system may be determined without great experimental difficulty, in an instrument of the type herein described.

Unfortunately, for the condensed region there is no satisfactory means of correlation of viscosity, pressure, and composition. Although the experimental work indicated a moderate percentage increase in viscosity with pressure in the condensed region for the experimentally covered pressure range, the widely varying volatilities of the lighter components greatly complicate any attempt at correlation. (See Figures XI and XII). The conclusion here is that more extended experimental studies may develop some satisfactory empirical correlation.

PHASE EQUILIBRIUM DATA

Since the experimental procedure has already provided a certain amount of data on bubble-point pressures for a limited composition range, it is of interest to present this additional information in the tentative diagram shown in Figure XIV. The curves represent the bubble-point pressure as a function of mass per cent methane for fixed mass ratios of propane to crystal oil. Data for the methane, propane curve were taken from previous work by Sage and co-workers (5). It should be noted that in the region 0% to 5% methane, for a fixed propane to crystal oil ratio the bubblepoint pressure is proportional to the per cent methane. indicating that Henry's law for methane is substantially true for the compositions in the range studied. However, the addition of propane to the methane crystal oil system markedly decreases the bubble point pressure. The change in Henry's law constant on addition of propane apparently is not proportional to either mass or mol per cent. If in the future a more extended study of this system is made, these tentative conclusions can be checked.

The Bubble-Point Pressure at 100°F. for the System Methane, Propane, Crystal Oil as Related to Composition.

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Moure XIV

LITERATURE CITED

(4) Sage, B. H., Sherborne, J. E., Lacey, W. N., Production Bulletin No. 216,
American Petroleum Institute.

APPENDIX

VISCOSITY OF CRYSTAL OIL C

^a Interpolated values.

VISCOSITY FOR THE EETHANE PROPANE CRYSTAL OIL SYSTEM

100° F.

Compositions² as Follows

e.

d

Compositions are calculated on a mass percent basis.

CO is the abbreviation for crystal oil C.

VISCOSITY FOR THE METHANE PROPANE CRYSTAL OIL SYSTEM

100° .

VISCOSITY FOR THE METHANE PROPANE CRYSTAL OIL SYSTEM

 100° F.

Compositions as Follows

VISCOSITY FOR THE METHANE PROPANE CRYSTAL OIL SYSTEM

100^0 F.

Compositions as Follows

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