THE GENERALIZED PHASE BEHAVIOR

OF

PARAFFIN-TETRALIN-BITUMEN SYSTEMS

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John S. Billheimer

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ABSTRACT

The addition of paraffin hydrocarbons to a solution of bitumen in tetralin will cause partial separation of the bitumen. Increasing the paraffin concentration will increase the separation of bitumen providing a second liquid phase characterized by high solvency for bitumen does not form. A maximum in the bitumen separation is thus obtained at the paraffin concentration corresponding to the formation of this second liquid phase. An increase in temperature generally results in a decreased separation of bitumen. These complex phase behaviors have been investigated for the addition of methane, n-pentane, and decane to a restricted bitumen-tetralin system.

PREFACE

Bitumen will separate from a solution of bitumen in tetralin upon addition of paraffin hydrocarbons. The investigation of the conditions causing this separation is presented in five parts divided according to the experimental methods applicable to the various systems and conditions. Part I presents the preparation and properties of a bitumen-tetralin solution. Part II concerns addition of paraffin hydrocarbons at atmospheric pressure in glass centrifuge tubes, whereas Part IIJ concerns similar operations performed in a pressure bomb at 200 psi absolute. Part IV introduces the formation of a second liquid phase and its effect upon the study of the separation of bitumen from the system. In Part V a vapor phase is obtained in the investigation of the guaternary system containing methane, decane, tetralin, and bitumen. In conclusion it is hypothesized that the discontinuities in the bitumen separation curves are a consecuence of the multiphase nature of the overall system and not specifically a property of the bitumen.

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SIMULATION OF NATURAL ASPHALT-ORUDE OIL SYSTEMS

BY A REFINED BITUMEN-TETRALIT SYSTEM

A bituminous material may separate under certain conditions occurring in the production of petroleum. The addition of the light hydrocarbons, methane through decane, favors the separation of this material. The separation of bituminous material from a Santa-Fe-Springs crude oil has been investigated by addition of methane, ethane, propane, iso-butane, n-butane, and n-pentane.(1) A similar investigation has been made with trap liquid from the Greeley Field upon addition of the associated trap $gas \cdot (2)$ In general, increasing the temperature reduces the separation of the bituminous material. However, the phase behavior of such natural bitumen-hydrocarbon systems is difficult to study quantitatively as the bituminous material which separates is not a simple substance. The Preparation of a Refined Bitumen

Orude bituminous material obtained from the South Coles Levee Field was subjected to an extensive purification process to yield a purified "bitumen." The crude material was leached three times with pentane at 220 deg F at the vapor pressure of pentane. The residue was dissolved in tetralin at 190 deg F and the insoluble foreign matter was separated by a centrifuge and discarded. Pentane was then added to the tetralin solution until the pentane concentration was 0.90-0.93 weight fraction of the mixture. Black, flocculent bitumen separated. It was centrifuged, washed with pentane,

PART I

and dried in an air bath at 120 deg F. The purification process was repeated three times. A "wax" separated when the first pentane liquor was cooled to 32 deg F. Evaporation of the subsequent pentane liquors produced a "resin." The ultimate analyses of these components are shown in Table I. The purified "bitumen" was obtained as shiny black particles. The specific gravity of the bitumen was 1.115 at 77 deg F compared to water at its maximum density. The particles were brittle, but apparently amorphous.

Prolonged agitation of this purified bitumen with tetralin at room temperature will produce a solution containing a maximum of 0.07 weight fraction bitumen. A tetralin solution containing 0.05 weight fraction bitumen was therefore proposed as simulated crude oil to investigate the conditions causing precipitation of the bitumen.

Materials

The tetralin used in these investigations was obtained from E. I. du Pont de Nemours and Company. The material was fractionated in a thirty-plate glass column at a pressure of approximately 1 psi. The initial and final 10 percent portions were discarded. The purified tetralin showed an index of refraction relative to the D line of sodium of 1.5401 at 77 deg F. Its specific volume was 0.016699 cu ft per 1b at 77 deg F.

The n-pentane was obtained from the Phillips Petroleum Company with an analysis which indicated that it contained less than 1 mole percent of material other than n-pentane, which was mainly iso-pentane. The n-pentane was used without further treatment for all operations associated with the purification of bitumen. However, supplies of n-pentane were fractionated at reduced pressure in a glass-ringpacked column for use in the majority of the measurements involved in the study of the restricted ternary system. The primary objective of the limited purification of the n-pentane was to remove the dissolved noncondensible gases such as nitrogen. The pertinent physical characteristics of the n-pentane were obtained from data available in the literature.(5.4)

The Bitumen-Tetralin Solution

Solutions of bitumen in tetralin prepared by saturation at temperatures exceeding 220 deg F contain greater than 0.10 weight fraction bitumen. Upon cooling they form a gel. A solution that is stable at room temperature can be obtained by dissolving 0.05 weight fraction bitumen in tetralin at 190 deg F and cooling to room temperature. The stability of a 0.05 weight fraction solution was established by preparation of tetralin solutions containing a maximum of 0.07 weight fraction bitumen through prolonged agitation at room temperature. Three days were required to reach this concentration by agitation of solid bitumen with tetralin at room temperature. To determine the rate of solution at various temperatures, samples of the liquid phase were taken after agitation of the solid bitumen with tetralin for definite intervals of time. Successive concentrations attained at the several temperatures are presented in Table II.

The solution rate constant (k) is assumed to be described by the first order rate equation $\frac{dC}{dT} = k(C_{\infty}-C)$. The weight fraction of bitumen in the liquid phase is represented by (C) at any time (T) and the weight fraction of bitumen in solution when the liquid phase is in equilibrium with the solid phase is represented by (C_{∞}) . Estimated values of the equilibrium solubility and the rate of solution constant are presented in Table III and Figure 1. The advantage of preparing solutions at elevated temperatures is evident.

The low rate of approaching equilibrium in the binary tetralinbitumen system at room temperature will later be found a controlling influence in the investigation of the pentane-tetralin-bitumen system at low concentrations of pentane. Since the solubility of bitumen in pentane has been determined to be of the order of 0.001 weight fraction bitumen, equilibrium difficulties will not be expected at high concentrations of pentane.

The Analytical Determination of Bitumen

When pentane is added to a solution of bitumen in tetralin at room temperature, bitumen separates from the solution. Experiment shows that when the pentane amounts to 0.90 to 0.95 weight fraction of the total mixture, substantially complete precipitation of the bitumen from the solution will be obtained. Noting that the solubility of bitumen in pure pentane at room temperature is less than 0.001 weight fraction, the precipitation of bitumen from tetralin solution by 0.90 to 0.95 weight fraction pentane is considered 99.9%

determination of bitumen.(5) In practice the sample is agitated with this concentration of pentane for two hours at room temperature and centrifuged at 1000 times the acceleration of gravity for 30 minutes. The separated bitumen is washed three times with pentane, then dried in an air bath at 120 deg F. Typical results obtained in the standardization of a tetralin solution containing 0.05 weight fraction bitumen are shown in Table IV.

The validity of this determination is also contingent on the homogeneity of the purified bitumen. It will be noted that the method of analytical determination is substantially the same pentane separation process employed in the original purification of the bitumen. If the purification has been sufficient, there should be no change in the ultimate analysis when the material is subjected to a further process of solution in tetralin and separation by pentane. This is confirmed by the following experiments:

Solid refined bitumen was leached with tetralin at 34 deg F and at 220 deg F. The bitumen was recovered from the tetralin extracts by the standard pentane precipitation. Table V compares the ultimate analysis of the bitumen from the extracts to the analysis of the material undissolved by the tetralin. Only a slight shift in the C:H ratio is observed between the first cold tetralin extract and the residue from an incomplete hot tetralin leaching. The hydrogen content in all cases differs not more than 0.3% from the average for two samples of the original refined bitumen.

The carbon contents in the wax and resin as shown in Table V

differ by 3 and 2 percent respectively from that of refined bitumen. Refined bitumen can therefore be considered as essentially a single component with regard to the process of solution in bitumen and separation by a high concentration of pentane at room temperature.

Conclusion

A refined bitumen can be obtained from the bituminous material occurring in crude petroleum by successive cycles of dissolving the material in tetralin and reprecipitating it by addition of pentane. The material obtained is essentially homogeneous with reference to extraction by tetralin and precipitation by pentane. A tetralin solution containing 0.05 weight fraction bitumen can be readily prepared by heating a mixture of bitumen and tetralin at 190 deg F. This solution will remain stable at room temperature. The rate of solution of solid bitumen in tetralin is exceedingly slow at room temperature, but solution proceeds at a practical rate at temperatures exceeding 160 deg F. A restricted system formed by this 0.05 weight fraction bitumen-tetralin solution with varying amounts of pentane will be investigated as a simplification of the natural bitumen-crude oil system. It is expected from the behavior of the binary bitumen-tetralin system that the ternary system with pentane will be very slow in attaining equilibrium when only small amounts of pentane are in the system.

PART II

THE PENTANE-TETRALIN-BUTUMEN AND THE DECANE-TETRALIN-PITUMEN SYSTEMS AT ATMOSPHERIC PRESSURE

The separation of an asphaltic phase from naturally occurring hydrocarbon mixtures upon the addition of natural gas or hydrocarbons of low molecular weight has been reported (1,2,6,7,8) The addition of pentane or decame to a solution of bitumen in tetralin results in a similar separation of the bitumen. For those temperatures and concentrations such that the vapor pressure of pentane or decame from the system does not significantly exceed one atmosphere, the operation may be performed in glass centrifuge tubes.

Experimental Methods

Pentane or decame was added gravimetrically to a glass centrifuge tube containing the bitumen-tetralin solution. The investigation has been restricted to systems containing bitumen and tetralin in the weight ratio of 1:19. The centrifuge tube was sealed and the mixture was mechanically shaken in an air bath at 70, 160 or 220 deg F for two hours. It was then centrifuged at approximately 1000 times the acceleration of gravity. Temperature could not be maintained entirely constant during the centrifugation, but tests indicated that the error so incurred was inappreciable. The liquid phase was decamted and discarded. The residue was washed three times with pentane, dried and weighed. A correction for the extraneous bitumen resulting from the occlusion of a portion of the liquid phase was calculated from the wet weight of the residue.

Experimental Results

The addition of pentane to the bitumen-tetralin-solution caused separation of bitumen as a solid or plastic phase. At 70 deg F and one atmosphere of pressure, separation of bitumen resulted when the concentration of pentane exceeded 0.2 weight fraction pentane in the total system. Table VI and Figure 2 show that the weight fraction of the total bitumen which separated increased when the pentane concentration was increased. Substantially "total" precipitation was accomplished when the pentane concentration exceeded 0.7 weight fraction of the entire system.

The decanted liquid phase was kept for a week and examined. No further precipitate was collected in the case that the pentane concentration exceeded 0.3 weight fraction of the total system. However, for lesser concentrations of pentane Table VII shows appreciable additional bitumen separated upon retaining the decanted liquid phase for a week. Thus equilibrium between the solid and liquid phases in the pentane-tetralin-bitumen system is not completely attained within two hours of agitation at 70 deg F. This slow attainment of equilibrium applies when the pentane concentration is less than 0.3 weight fraction of the total system. Furthermore, a correction must be made for the bitumen contained in the liquid phase occluded in the precipitate. This correction increases in relative magnitude as the quantity of precipitate decreases while the bitumen concentration of the liquid phase is correspondingly increasing. Table VIII indicates that the correction for bitumen in the occluded liquid phase becomes of the same order of magnitude as the true bitumen precipitate when the pentane concentration is decreased to 0.2 weight fraction of the total system.

Thus the large relative errors when the fraction of the total bitumen separated is small prevent the direct experimental determination of the minimum concentration of pentane capable of causing separation of bitumen from this system. This region of the phase diagram is therefore studied indirectly by considering the ratio of bitumen to tetralin in the liquid phase of the ternary system in equilibrium with solid bitumen as a continuous function of the concentration of pentane. As the concentration of pentane is reduced, this ratio must approach the value prevailing in the binary system in equilibrium with solid bitumen at that temperature. The ratio of bitumen to tetralin in the saturated binary system at any temperature can be calculated from Table VI. The ratio of bitumen to tetralin in the liquid phase is plotted in Figure 3 for the experimentally satisfactory systems containing pentane in excess of 0.25 weight fraction of the total system. Semi-logarithmic coordinates are used for convenience of scale. This curve is then ex-. tended to the ordinate intercept which corresponds to a saturated binary system at that temperature.

Considering the total system containing 0.05 weight fraction bitumen, the ratio of bitumen to tetralin is restricted to 0.0525

in the system as a whole. Thus any concentration of pentane for which the allowable ratio of bitumen to tetralin in the liquid phase is less than 0.0525 will necessitate separation of bitumen from that liquid phase. The intersection of this curve with 0.0525 then corresponds to the threshold concentration for pentane; i. e., for any higher pentane concentration, separation of bitumen should occur.

This threshold concentration of pentane is transposed to form the abscissa intercept of Figure 2. This permits completion of the bitumen separation curve for low concentrations of pentane. It is noted that in this region of high average molecular weight, the experimental bitumen separation is consistently less than that implied from equilibrium considerations. This is ascribed to a greater role of surface energies in this region than occurs in the systems of higher paraffin content.

In similar experiments, decane was shown to be slightly more effective than pentane in causing separation of bitumen from the liquid phase. Table IX and Figure 4 show that decane causes substantially total precipitation of the bitumen when the decane concentration exceeds 0.50 weight fraction of the total system at 70 deg F and one atmosphere pressure. When the temperature was increased to 160 deg F, precipitation was substantially total at 0.7 weight fraction of decane. However at 220 deg F., the same decane concentration permits 0.04 weight fraction of the total bitumen to remain in the liquid phase. The threshold intercepts for these bitumen separation curves have been obtained from Figure 5 in the manner described above for the case of pentane at 70 deg F.

PART TII

THE ATTAINMENT OF EQUILIBRIUM IN THE PENTANE-TERRALIN-BITUMEN SYSTEM AT 200 PEL ARECUUTE

The separation of bitumen from the pentane-tetralin-bitumen system has been previously described only for 70 deg F. Then the temperature was increased to 160 or 220 deg F, it became necessary to employ a pressure bomb. A pressure of 200 psia was selected as sufficient to avoid the formation of a gaseous phase. Nomb techniques do not permit storing of the decanted liquid phase at the operating conditions to determine the attainment of equilibrium. Therefore special techniques were employed to determine the time necessary to attain equilibrium.

Experimental Method

The stainless steel weighing bomb described in a previous paper of this laboratory was employed.(1) This bomb had been especially designed to permit centrifugation and displacement of the phases while maintaining constant pressures up to 10,000 psi4. Bitumentetralin solution was introduced into the evacuated bomb and the weight of solution taken was obtained by difference. Pentane was then introduced into the bomb at the desired temperature until a pressure of 200 psia was obtained. Pressures were measured by a pressure balance accurate to \pm 1 psia in the 200 psia range. The bomb was subsequently cooled to room temperature and the weight of pentane obtained by difference. Determination of the rate of heat transfer to the bomb from the air thermostat indicated the time required to restore the system to operating temperature. The cooling of the bomb during subsequent manipulations was estimated from dooling curves of the bomb to not affect the temperature of the liquid system more than 2 deg F.

The bomb was mechanically agitated for 25, 10, or 4 hours for 70, 160, and 220 deg F respectively. The relative periods of agitation were estimated from the rate constants for the dissolving of bitumen in tetralin given in Figure 1. After sufficient agitation, the bomb was centrifuged at 10,000 RPM within the thermostat. After centrifugation, the liquid phase was displaced from the bomb by a source of mercury at a pressure controlled within ± 3 psia.

Experimental Results

Table X and Figure 2 give the weight fraction of the total bitumen separated for various concentrations of pentane at 160 and 220 deg F. The threshold intercept is obtained as described previously. The relation of the separation of bitumen by pentane at 160 and 220 deg F to the separation at 70 deg F is approximately the same as that described above for decane.

To determine the weight of pentane introduced, it had been necessary to cool the bomb from the addition conditions. A few experiments were performed transferring the pentane from an auxiliary weighing bomb in an attempt to avoid the effect of cooling on the precipitation equilibrium. In these experiments, the temperature was maintained constant throughout the addition, agitation, centrifugation, and displacement.

To determine whether equilibrium was attained, the liquid phase was in this case displaced into another evacuated bomb. The agitation, centrifugation, and displacement process was then repeated. Finally, when it was believed that equilibrium had been reached after the fourth cycle, the displaced solution was allowed to cool to room temperature. It was then restored to operating temperature for two hours, centrifuged, and displaced. This is analogous to the cooling necessary for weighing in the normal procedure. The weight of bitumen retained in the bomb in this case is shown by Table XI to be of the same order of magnitude as that obtained in each of the four "equilibrium" steps above, after the one hour primary period. Furthermore this was approximately the amount of bitumen retained on the bomb walls when the process was repeated without centrifugation. It appears therefore that the bitumen obtained in the equilibrium and reconditioning operations, excluding the primary, is simply that obtained from solution adhering to the bomb walls. It is therefore concluded that for temperatures of 160 and 220 deg F and pentane concentrations exceeding 0.3 weight fraction, the separation of bitumen attains a rapid and reversible equilibrium.

At room temperature however, the laws of simple solution are invalidated by apparently significant surface energies. Table XII indicates that reversible equilibrium cannot be attained. At

70 deg F and a pressure of 8000 psia with 0.535 weight fraction pentane, 0.334 weight fraction of the total bitumen separated after 19.5 hours of agitation. An additional 0.311 weight fraction of the total bitumen was obtained after 21 hours of further agitation. However, under similar conditions a continuous agitation of 36.5 hours yielded a bitumen separation of 0.210 weight fraction. It will be noted that this result is comparable to the first of the above agitation periods only, instead of the expected separation comparable to the sum of that obtained in the two 20 hour periods. It is thus concluded that simple solution laws reasonably describe the pentane-tetralin-bitumen system for temperatures not less than 160 deg F, and concentrations not less than 0.3 weight fraction of pentane in the system. At low temperatures and high average molecular weights of the system, surface energies and low equilibrium rates invalidate simple solution measurements.

PART IV

THE FORMATION OF A SECOND LIQUID PHASE IN THE PENTANE-TETRALIN-BITUMEN AND DECANE-TETRALIN-BITUMEN SYSTEMS

As many as four phases have been caused to separate from a crude oil by the introduction of a natural gas or propane at 70 deg F and 1500 psia.(1) At least one phase was a liquid sub- $^{
m O}$ stantially free of components of high molecular weight. The separation of an asphaltic phase from a Santa Fe Springs crude oil resulted from the introduction of methane and the separation reached a maximum between 0.14 to 0.19 weight fraction of methane in the system. Ethane gave similar results.(1) The decline in the separation of this asphaltic phase with further increase in concentration of the paraffin hydrocarbon was accompanied by the appearance of an additional condensed phase consisting of a dense, viscous liquid. This liquid had a distinctly higher specific gravity and average molecular weight than the normal liquid phase (2) A similarity between the separation of bitumen in the field and the separation of asphalts from lubricating oil cuts has been reported . (9)

Experimental Observations

This second liquid phase has been obtained under certain conditions in the pentane-tetralin-bitumen and decane-tetralin-bitumen systems at 8000 psis. Towards the end of the displacement for large hydrocarbon concentrations, the displaced fluid may suddenly change

from a low viscosity fluid to a dense viscous mass extruding from the bomb. This dense viscous phase was obtained very conclusively as shown in Figures 6 and 7 at 160 deg F with either pentane or decane in concentrations exceeding 0.5 weight fraction hydrocarbon in the total system at 8000 psia. The second liquid phase was also obtained with pentane concentrations exceeding 0.5 weight fraction at 200 psia for 160 deg F only. In the case of decane at 8000 psia and 0.4* weight fraction decane, the shapeless viscous flowing mass shown in Figure 8 was obtained. In the case of 0.6 weight fraction hydrocarbon, Figure 9 shows the second liquid phase extruded from the bomb in a consistency retaining its form when collected in a glass centrifuge tube. With pentane at 8000 psis at both 0.4 and 0.6 weight fraction hydrocarbon, second liquid phase of extrudable consistency was obtained. At 200 psia, the same extrudable material was obtained for 0.6 weight fraction pentane, but at 0.4 weight fraction pentane a second liquid phase did not appear. No determinations were made with decane at 200 psia, but at atmospheric pressure in glassware, the formation of only a slight amount of this second liquid phase was observed.

When the temperature was increased to 220 deg F., only a small quantity of a second liquid phase was obtained for 0.4 and 0.6 weight

* Hydrocarbon concentrations in the range 0.35 to 0.45 are referred to as 0.4 weight fraction, and the range 0.55 to 0.65 as 0.6 weight fraction for simplicity in the discussion of the system.

fraction decane at 8000 psia, and at atmospheric pressure the formation of a second liquid phase was questionable. For all pentane concentrations at 220 deg F and both 200 and 8000 psia, the supernatant fluid was followed immediately by the displacement mercury, no second liquid phase being observed.

At 70 deg F, a second liquid phase in the consistency of a viscous fluid similar to Figure 8 was obtained for both 0.4 and 0.6 weight fraction decane at 8000 psia. The viscous phase and appeared in small quantities at atmospheric pressure. Pentane at 8000 psia and 70 deg F produced a large quantity of the viscous fluid at a concentration of 0.6 weight fraction hydrocarbon. A lesser amount of viscous fluid was obtained at 0.4 weight fraction pentane. A second liquid phase was not observed upon addition of pentane at 70 deg F and atmospheric pressure.

It is generalized from Tables XIII and XIV that the ratio of second liquid phase to the total liquid phases increases with the concentration of hydrocarbon for a given temperature. For a given concentration of hydrocarbon, decane appears more favorable to formation of a second liquid phase than pentane. In all cases the formation of a second liquid phase was accompanied by a decline in the fraction of the total bitumen separated in the bomb. This is shown by the negatively sloped solid lines on the right side of Figures 6 & 7 which represent the fraction of the total bitumen that separates in the bomb. The dashed lines in Figures 6 & 7 represent the sum of the bitumen retained in the bomb and the bitumen in solution in the second liquid phase. Obviously, the difference of this sum from unity represents the weight fraction of the total bitumen remaining in the first liquid phase. It is apparent from the figures that the advent of a second liquid phase causes no discontinuity in the concentration of bitumen in the first liquid phase.

These results are of the same type as those reported by Botkin and $\operatorname{Reamer}_{(1,2)}$ if it be recognized that the plastic phase they obtained with crude bitumen corresponds essentially to the solid bitumen which separates in the bomb for the purified bitumen eystem, and their dense liquid corresponds in the purified system to the complete range from viscous fluid to extrudable mass. However, they obtained the second liquid phase only for methane and ethane at all temperatures including 220 deg F and at no temperature for propane, butane, or pentane.

It appears probable that the behavior encountered in the less refined systems, using crude bitumen, is limited to systems where substantially large quantities of hydrocarbons of relatively low molecular weight are present. The additional liquid phase is generally abtained at high pressures and at temperatures below 220 deg F for a hydrocarbon concentration exceeding 0.4 weight fraction. The consistency of this additional phase varies from semi-plastic at 160 deg F to viscous fluid at 70 deg F. The high bitumen content of this dense liquid results in a maximum in the precipitation of solid bitumen at the incidence of its formation.

Quantitative Results

The data for the measurements carried out at a pressure of 8000 psia are presented in Figures 6 and 7 and Tables XIII and XIV for both the pentane-tetralin-bitumen and the decane-tetralin-bitumen The same method was used to determine the threshold points systems. for these measurements as was previously explained in connection with Figures 2 & 3. The systems are compared at low pressures in Figure 10 at a temperature of 70 deg F and a pressure of 15 psia. The effectiveness of decane in causing separation of bitumen is substantially equal to that of pentane at low hydrocarbon concentrations. At higher concentrations the decane appears somewhat more effective. At a temperature of 220 deg F, data on the pentane system is unavailable at 15 psia due to the vapor pressure of the pentane, so comparison is made between decane at 15 psia and pentane at 200 psia. Taking note of the pentane 8000 psia separation line, it would appear that at a temperature of 220 deg F decane is more effective than pentane at comparable low pressures.

In the decane-tetralin-bitumen system an inversion of the effect of temperature on the separation is noted in Figure 5 for a pressure of 8000 psia. The inverted effect of temperature on the separation caused by decane is compared in Figure 11 to the normal decrease in separation upon increase in temperature obtained with pentane. A similar inversion of the effect of temperature on asphalt separation is reported in a California Research Corporation paving-asphalt process.(10) Since the inversion does not occur in the corresponding pentane system, the temperature sequence of the decane isotherms must reverse before intersecting the ordinate representing the binary bitumen-tetralin system. Due to this temperature inversion in the decane system at 8000 psia, no direct comparison of hydrocarbon effectiveness is made at high pressures.

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PARTY

MULTIPHASE REHAVICE OF A RESTRICTED METHANE-DECAME-

TETRALIN-BITUMEN SYSTEM

Introduction of methane into a restricted decane-tetralinbitumen system simulates the natural asphalt-crude oil-trap gas systems investigated by Botkin, Reamer et al.(1,2) At the 8000 psia operating pressure used in the previous investigation, the solubility of methane in a methane-tetralin-bitumen system is not sufficient to separate significant quantities of bitumen. Consequently in this investigation various amounts of methane have been added to a decane-tetralin-bitumen system restricted to the proportions 2:19:1. The proportion of decane was selected as the maximum for which thed**ecan**e-tetralin-bitumen solution would be stable at 70 deg F and one atmosphere **pr**essure.

The proportion of methane has been varied from the dew point to the bubble point at a pressure of 8000 psia and a temperature of 220 deg F. A limited number of determinations at the same pressure were also made at 70 deg F. A maximum in the separation of bitumen was obtained similar to that reported in Part IV for the decane-tetralin-bitumen system. In addition a minimum in the bitumen separation was obtained for a methane concentration between that of the separation maximum and the dew point.

Experimental Method

The experimental method presented in Part III of this paper was used for this system. However, the partial volumetric data were not available for estimating the proportions of the restricted decane-tetralin-bitumen solution and of methane to obtain a desired concentration of methane in the system. In the early determinations this was estimated from the following information:

(a) The partial volume of methane in the methane-decane system at 8000 psia, 100 and 220 deg $F_{(11,12)}$ applied as a func-tion of the methane concentration,

(b) The partial volume of decane in the above system applied as a function of the sum of the decane and tetralin concentrations,

(c) The partial volume of benzene in the methane-benzene system at pressures up to 5000 psia and a temperature of 100 deg F(13,14).

(d) The ratio of the specific volume of tetralin to that of benzene at 77 deg F and one atmosphere pressure.

The actual methane concentrations obtained by means of this estimation from partial volumetric data for the first three determinations at 70 deg F were $0.015 \stackrel{+}{=} 0.003$ weight fraction of the system lower than expected. For the first two determinations at 220 deg F the actual methane concentrations obtained were $0.05 \stackrel{\pm}{=} 0.01$ weight fraction of the system lower than intended. Using these empirical corrections, subsequent bomb loadings were within $\stackrel{\pm}{=} 0.01$ weight fraction of the methane concentration desired.

The composition of the vapor phase was determined by measuring

the methane through a wet test gas meter and collecting the less volatile components in a dry ice-acetone trap. The concentrations of decane and tetralin in this condensate were found by refractive index measurements. No appreciable amount of bitumen was obtained from the vapor phase. It was assumed that only negligible amounts of volatile components were present in the separated bitumen phase. The composition of the liquid phase was therefore calculated by difference from the total composition of the system.

The calculation of the liquid phase composition by means of refractive index data on the condensate was later confirmed by C. Yundt using gravimetric analysis based on the specific volume of the liquid phase and knowledge of the partial volumes of decane, tetralin, and bitumen at that state. Data on two samples analyzed by both methods are presented in Table XV.

The materials are the same as reported in Part I of this paper except that a new bitumen preparation was used for the latter portion of the investigation. The new bitumen was prepared as previously except that a three-day soxhlet extraction with pentane was added as a final step in the preparation. Table XVI indicates that the carbon-hydrogen ratio was decreased slightly in the second preparation. Figure 12 shows that the separation of bitumen from the decane-tetralin-bitumen solution upon the addition of methane is similar in behavior for the two bitumen preparations, but that the latter bitumen preparation is slightly less soluble at a given state 24

of the system.

Experimental Results

The weight fraction of the total bitumen present that separates as a solid phase is presented in Figure 12 as a function of the weight fraction of methane in the total system. A maximum was obtained in the fraction of the total bitumen which separated as a solid phase when the methane concentration was 0.3 weight fraction of the total system. This is **anal**ogous to the behavior previously cited for the pentane-tetralin-bitumen and the decane-tetralinbitumen systems.

The compositions of the phases for various states of the system from the bubble point to the dew point are given in Table XVII. The composition of the liquid phase is presented in Figure 13 as a function of the weight fraction methane in the total system. The maximum in the separation of bitumen in Figure 12 corresponds to the minimum in the solubility of bitumen in the liquid phase in Figure 13. It is evident that this minimum solubility of bitumen correlates with the maximum in the sum of the concentrations of decane and tetralin in the liquid phase. The solubility of bitumen in the liquid phase is thus related inversely to the concentration of methane in the liquid phase as shown in Figure 14.

The solubility of bitumen in the liquid phase expressed as grams of bitumen per gram of volatile material is presented in Table XVIII as a function of the average molecular weight of the liquid phase. For this purpose the molecular weight of the bitumen was taken as 1000 although its value has been variously reported as 1000 to 4000.(1.2) Equilibrium "constants" for the distribution of methane, decane, and tetralin between the gas and liquid states are also presented in Table XVIJI. The equilibrium constants are given in Figure 15 as a function of the weight fraction of methane in the total system. The apparently irregular separation curves for bitumen in the methane-decane-tetralinbitumen system are thus reduced to continuous functions when the solubility of bitumen in the liquid phase is plotted with reference to the composition of the liquid phase rather than that of the total system. The discontinuities of the curves of bitumen separation as a function of the composition of the sytem thus appear to be chiefly a consequence of the phase relations of the methane-decane-tetralin-system and not directly a property of the bitumen.

Under conditions of 70 deg F and 2000 psia, a second liquid phase was obtained from the restricted methane-decane-tetralinbitumen system. The second liquid phase was similar in nature to that previously reported from the pentane-tetralin-bitumen and decane-tetralin-bitumen systems at certain states. Table XIX indicates that this second liquid phase was associated with the maximum in the separation of bitumen analogous to the maximum previously reported for the corresponding pentane and decane systems. The data are of preliminary nature and insufficient to

warrant graphical presentation. In the more extensive work at 220 deg F already presented, the occurrence of a second liquid phase is suspected by analogy to be associated with the maximum observed in the separation of bitumen. However the flashing of methane from the phase displacement tube makes it impossible to detect a liquid phase change if it were to occur in the methane system investigations at 220 deg F.

Conclusion

Asphaltic bitumen is quite soluble in tetralin but relatively insoluble in aliphatic hydrocarbons. Addition of methane, pentane, or decane, to a tetralin solution of bitumen will cause precipitation of the bitumen as a solid phase. In general the separation of bitumen increases with the addition of aliphatic hydrocarbon. However, under certain conditions, especially at high pressures, the separation of solid bitumen reaches a maximum and decreases upon further addition of aliphatic hydrocarbon.

It appears that the maximum separation of solid bitumen is related to a change in the nature of the liquid phase. When the solubility of bitumen in the liquid phase is taken as a function of the composition of the liquid phase itself rather than that of the total system, a continuous function is obtained. Due to the experimental technique being inadequate to separate the two liquid phases under all conditions where they occur, the overall composition of the liquid phases is used in these correlations.

The continuity of the bitumen solubility when referred to the composition of the liquid phase is shown in Figures 3, 5, and 14 for pentane, decane, and methane as the aliphatic constituent respectively. Any study of the apparent solubility of bitumen in hydrocarbon systems must therefore take cognizance of the phase behavior of the other components.

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FIGURES

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- Figure 1. The solution of bitumen in tetralin at atmospheric pressure.
- Figure 2. Separation of bitumen from restricted pentane-tetralinbitumen system at low pressures.
- Figure 3. Composition of liquid phase in restricted pentanetetralin-bitumen system at equilibrium with solid bitumen 70 deg F, atmospheric pressure.
- Figure 4. The separation of bitumen as a plastic phase from decane-tetralin-bitumen system at atmospheric pressure at a weight ratio of bitumen to tetralin of 0.0525.
- Figure 5. Composition of the liquid phase in restricted decanetetralin-bitumen system in equilibrium with solid bitumen.
- Figure 6. Separation of the bitumen from the pentane-tetralinbitumen system at 8000 psia.
- Figure 7. Separation of bitumen from the decane-tetralin-bitumen system at 8000 psia and a weight ratio of bitumen to tetralin of 0.0525.
- Figure 8. The nature of the second liquid phase obtained from the decane-tetralin-bitumen system containing 0.4 weight fraction decane and 0.0366 weight fraction bitumen at 160 deg F, 8000 psia.
- Figure 9. The nature of the second liquid phase obtained from the decane-tetralin-bitumen system containing 0.6 weight fraction decane and 0.0549 weight fraction bitumen at 160 dec F, 8000 psia.
- Figure 10. Comparative separation of bitumen from the pentane-tetralinbitumen and the decane-tetralin-bitumen systems.
- Figure 11. Comparative influence of temperature upon separation of bitumen from the pentane-tetralin-bitumen and decane-tetralin-bitumen systems containing 0.35 weight fraction paraffin and 0.032 weight fraction bitumen.

- Figure 12. The weight fraction of the total bitumen separated as a solid phase at 8000 psia and 220 deg F as a function of the weight fraction methane in the total system.
- Figure 13. The composition of the liquid phase in equilibrium with solid bitumen at 8000 psis and 220 deg F.
- Figure 14. The solubility of hitumer in the liquid phase at 8000 psis and 220 deg F as a function of the weight fraction methane in the liquid phase.
- Figure 15. Equilibrium constants for methane, decane, and tetralin in the restricted quaternary system with bitumen at 8000 psia and 220 deg F.



Fig. 1 The solution of bitumen in tetralin at atmospheric pressure.





Fig. 1 The solution of bitumen in tetralin at atmospheric pressure.



Fig. 2 Separation of bitumen from restricted pentane-tetralin-bitumen system at low pressures.



Fig. 5 Composition of the liquid phase in restricted decane-tetralin-bitumen system in equilibrium with solid bitumen.



Fig. 6 Separation of the bitumen from the pentanetetralin-bitumen system at 8000 psia.



Fig. 7 Separation of bitumen from the decane-totr tetralin-bitumen system at 8000 psia and a weight ratio of bitumen to tetralin of 0.0525.



Fig. 8 The nature of the second liquid phase obtained from the decane-tetralin-bitumen system containing 0.4 weight fraction decane and 0.0366 weight fraction bitumen at 160 deg F, 8000 psia.



Fig. 11 Comparative influence of temperature upon separation of bitumen from the pentane-tetralinbitumen and decane-tetralin-bitumen systems containing 0.35 weight fraction paraffin and 0.032 weight fraction bitumen.



Fig. 12 The weight fraction of the total bitumen separated fis a solid phase at 8000 psia and 220 deg F as a function of the weight fraction methane in the total system.





Fig. 14 The solubility of bitumen in the liquid phase at 8000 psia and 220 deg F as a function of the weight fraction methane in the liquid phase.



Fig. 15 Equilibrium constants for methane, decane, and tetralin in the restricted quaternary system with bitumen at 8000 psia and 220 deg F.

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- TABLE II THE CONCENTRATION OF PITTINEN IN THE ITOUD PHASE IN PRECIMPE OF COLD PITTINEN FOR VARIOUS PERIODS OF OCT-TACT.
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THE ULTIMATE ANALYSES OF THE CONSTITUENTS SEPARATED FROM

CRIDE BT MUMEN

Constituent . Weight fraction of constituent

	Carbon	Hydrogen	Nitrogen	Sulfur	Ash to	Wt. Ratio of Carbon Hydrogen	to
Wax (a) Resin (b) Pitumen (c)	0.8481 0.8373 0.8208	0 .1283 0.0997 0.0742	0.0090 0.0185 0.0119	0.0120 0.0160	0.0120 0.0043	6.61 8.40 11.07	

- (a) Max is defined as the constituent insoluble in pentane at the ice point.
- (b) Resin is defined as the constituent obtained from evaporation of the pentane extracts.
- (c) Bitumen is defined as the constituent insoluble in pentane at 220 deg F.

TABLE II

THE CONCENTRATION OF BITUMEN IN THE LIQUID PHASE IN THE PRESENCE

OF SOLID BITUMEN FOR VARIOUS PERIODS OF CONTACT

Temperature	Time of Contact	Bitumen Conc. of	Nature of Liqu	uid Phase
	(hours)	Liquid Phase	At Temp. Cited	After Cooling
34	24 73	0.0174 (a)	Liquid Soln	Liquid Soln
78	8 24	0.0533	Liquid Soln	Liquid Soln
130	72 4 11	0.0847 0.0805 0.0804	Liquid Soln	Liquid Soln
160	24 2 8	0.0866 0.0633 0.0841	Liquid Soln	Sl. Viscous Soln
190	21•5 1 4	0.0910 0.0912 0.0943	Sl. Viscous Soln	Viscous Soln
220	14 1 3	0.1008 0.1349 0.1152	Viscous Soln	Very Viscous Soln
250	11 5	0.1330 0.1930	Viscous Soln	Plastic Mass

(a) Weight fraction bitumen

TABLE III

THE EQUILIBRIUM SOLUBILITY OF BITUMEN IN TETRALIN CALCULATED

ACCORDING TO A FIRST ORDER RATE EQUATION

.

Temperature (deg F)	Times of Contact (hours)	Rate Constant (hours ⁻¹)	Equilibrium Concentration (weight fraction)
34	24.73	0.0073	0.0700
78	8,24	0.0214	0.0830
130	11,24	0.0426	0.0950
160	8,21.5	0.0660	0.1030
190	4,14	0.0760	0.1200
220	3,11	0.1135	0.1450

TABLE IV

COMPARISON OF DETERMINATIONS OF COMPOSITION OF

TETRALIN-BITUMEN SOLUTIONS

As Prepared	Weight	Fraction	by Pentane	Precipitation
				(Average)
0.0513 (a)	0.0524	(b)	0.0519 (b)	0.0522
0.0500	0.0508	•	0.0508	0.0508
0.0499	0.0511		0.0505	0.0508
0.0499	0.0516		0.0520	0.0518

- (a) Established from gravimetric measurements made in course of preparing solutions.
- (b) Duplicate determinations by pentane precipitation procedure..

TABLE V

COMPOSITION OF BITUMEN AFTER REPEATED EXTRACTION

τ**ύ**

	Carbon	Hydrogen	Nitrogen	W1 of n Ash to	t. Ratio Carbon Hydrogen
Bitumen before extraction					
with tetralin	0.8254(a)0.0789	0.0070	0.0003	10.48
Bitumen dissolved at 34 deg F	0.8144	0.0789	0.0058	0.0002	10.32
Bitumen dissolved at 220 deg F	0.8250	0.0753	0.0050	0.0001	10.96
Residual Bitumen (b)	0.8482	0.0772	0.0094		11.00

- (a) Weight fraction.
- (b) Undissolved residue after extraction by tetralin at 220 deg F.

TABLE VI

THE SEPARATION OF BITUMEN FROM THE PENTANE-TETRALIN-BITUMEN SYSTEM

AT 70 DEG F AND ATMOSPHERIC PRESSURE (a)

Weight	Weight			
Fraction	Fraction	Composition	of the Liquid	Phase
Pentane	Bitumen			
	Separated	Pentane	Bitumen	Tetralin
0.208	0.483 (b)	0.210 (c)	0.0240 (c)	0.766 (c)
0.213	0.484	0.218	0.0153	0.766
0.233	0.527	0.237	0.0188	0.744
0.239	0.547	0.244	0.0170	0.739
0.242	0.597	0.248	0.0155	0.736
0.253	0.632	0.259	0.0139	0.727
0.271	0.730	0.277	0.0103	0.712
0.273	0.599	0.277	0.0197	0.703
0.286	0.634	0.292	0.0133	0.6930
0.289	0.760	0.297	0.0089	0.6940
0.375	0.727	0.384	0.0086	0.6074
0.399	0.883	0.407	0.0075	0.5855
0.399	0.753	0.408	0.0076	0.5840
0.437	0.891	0.448	0.0031	0.5489
0.450	0.849	0.462	0.0042	0.5340
0.494	0.906	0.507	0.0024	0.4906
0.501	0.960	0.513	0.0010	0.4860
0.506	0.911	0.516	0.0021	0.4810
0.600	0.981	0.610	0.0004	0.3896
0.605	0.965	0.616	0.0007	0.3830
0.606	0.978	0.620	0.0004	0.3790
0.668	1.000	0.679	0.0000	0.3210
0.709	1.000	0.719	0.0000	0.2810
0.801	1.000	0.809	0.000	0.1910
0.803	1.000	0.812	0.0000	0.1890
0.890	1.000	0,895	0.0000	0.1050

- (a) Data limited to systems containing a weight ratio of bitumen to tetralin of 0.0526.
- (b) Weight fraction of the total bitumen which has separated after a period of 7 days at 70 deg F under quiescent conditions.
- (c) Weight fraction of the component in the liquid phase in equilibrium with the plastic or solid phase.

TABLE VII

INFLUENCE OF TIME UPON SEPARATION OF BITUMEN AT LOW PENTANE

WEIGHT FRACTIONS

Weight Fraction Pentane	Bitumen Separated in 2 hours	Additional Bitumen Separated in one week	Total Bitumen Separated	Recovery of Bitumen in 2 hours (percent)
0.271	0.730	0.000	0.730	100.0 (a)
0.253	0.632	0.000	0.632	100.0
0.242	0.427	0.170	0.597	71.5
0.239	0.335	0.212	0.547	61.2
0.213	0.198	0.286	0.484	35.2
0.208	0.168	0.315	0.483	23.6

(a) Recovery of bitumen in 2 hours compared to the total obtained after one week.

TABLE VITI

THE CORRECTION FOR EXTRANEOUS BITUMEN RESULTING FROM OCCLUSION

OF A PORTION OF THE LIQUID PHASE

Weight Fraction Pentane	Apparent Bitumen Separated (a)	Corrected Bitumen Separated	Occlusion Correction (percent)
0.606 (b)	0.990 (c)	0.978 (c)	1.2
0.399 (b)	0.834	0.753	10.8
0.286 (b) 0.273	0.752 0.753	0.634 0.599	18.6 25.7
0.271	0.880 0.836	0.730 0.632	20.6 32.1
0.242	0.810	0.597	35.8
0.233	0.788	0.527	49.6
0.215	0.828	0.483	69.2 71.7

- (a) Total bitumen separated before applying a correction for the bitumen content of the occluded liquid phase.
- (b) Representative values from Table VI; below 0.273 weight fraction pentane all experiments are reported in this table.
- (c) Weight fraction of the total bitumen in the system.

TABLE IX

THE SEPARATION OF BITUMEN AS PLASTIC PHASE FROM THE RESTRICTED DECANE-TETRALIN-BITUMEN

SYSTEM AT ATMOSPHERIC PRESSURE

Con (position of Weight Fract	System .ion)	Weight Fraction Bitumen	Compositic (on of the Lic Weight Fract	quid Phase sion)
Decane	Tetralin	Bitumen	Separated	Decane	Tetralin	Bitumen
			70 Deg F	ž.		
0.313 0.400 0.504 0.602	0.653 0.570 0.471 0.378	0.0344 0.0300 0.0248 0.0199	0.733 0.911 1.000 1.000	0.321 0.411 0.516 0.614	0.670 0.587 0.484 0.386	0.0093 0.0028 0.0000 0.0000
			160 Deg F			
0.099 0.199 0.249 0.298 0.403 0.600 0.800	0.856 0.761 0.713 0.667 0.567 0.380 0.190	0.0450 0.0400 0.0376 0.0351 0.0299 0.0200 0.0100	0.001 0.001 0.397 0.521 0.837 0.973 0.996	0.098 0.199 0.252 0.303 0.413 0.611 0.807	0.856 0.760 0.725 0.679 0.582 0.388 0.192	0.0459 0.0406 0.0227 0.0176 0.0050 0.0005 0.0002
			220 Deg F			
0.248 0.280 0.297 0.347 0.398 0.598 0.599	0.714 0.684 0.668 0.620 0.572 0.382 0.381	0.0376 0.0360 0.0352 0.0326 0.0301 0.0201 0.0200	0.019 0.477 0.456 0.582 0.760 0.942 0.892	0.248 0.289 0.306 0.356 0.410 0.610 0.611	0.714 0.702 0.685 0.636 0.588 0.389 0.389	0.0380 0.0089 0.0088 0.0077 0.0013 0.0005 0.0003

TABLE X

THE SEPARATION OF BITUMEN AS PLASTIC PHASE FROM

THE RESTRICTED PENTAME-TETRALIN-BITUMEN SYSTEM AT 200 PSIA

Weight Fraction	Weight Fraction Bitumen	Composition of the Liquid Phase (Veight Fraction)			
rentuane	Separated	Pentane	Bitumen	Tetralin	
		160 DEG F 200 F	STA		
0.285 (a) 0.386 0.553	0.242 (b) 0.659 0.454	0.267 (c) 0.393	0.0267 (c) 0.0111	0.686 (c) 0.595 (d)	
		220 DIG F 200 F	SIA		
0,240 0,320 0,591	0.017 0.220 0.843	0.241 0.322 0.600	0.0373 0.0267 0.0034	0.722 0.651 0.396	
(a) Weight	fraction pent	ane in the syst	tem.		

- (b) Weight fraction of the total bitumen separated as plastic phase.
- (c) Weight fraction of the component in the liquid phase in equilibrium with the plastic phase.
- (d) As a result of the formation of a second liquid phase at this state, the composition of the liquid phase was not determined.

TABLE XI

THE APPARENT BITUMEN SEPARATED FOR SUBSEQUENT

PERIODS OF AGITATION

Temperature, de	og F. 22	20	10	50	10	50
Pressure, psia	20	00	20	00	20	00
Pentane, wt. fi	· · 0.4	40	0.2	27	0.	38
Displacement	Agitation (hours)	Bitumen Sep'd (gms)	Agitation (hours)	Bitumen Sep'd (gms)	Agitation (hours)	Bitumen Sep'd (gmø)
First	1	0.927	0.6	0.006	0.4	1.056
Second	4	0.004	1.1	0.014	1.2	0.013
Third	11	0.010	5.8	0.031	3•7	0.017
Fourth	23	0.018	21.5	0.045	7.1	0.034
"Reconditioned"	'(a)	0.006		0.059		0.068
"No centrifugat	tion"(b)	0.007		0.083	a 144	0.072

- (a) Reconditioning refers to the process wherein the displaced solution was allowed to cool to room temperature, then restored to operating temperature for two hours, centrifuged, and displaced.
- (b) No centrifugation refers to the process wherein the liquid phase was displaced into another evacuated bomb, and immediately displaced from this bomb without any centrifugation having been applied.

TABLE XII

THE INVALIDITY OF SIMPLE SOLUTION LAWS

FOR THE SEPARATION OF BITUMEN AT 70 DEG F AND 8000 PSIA

Pentane Conc.	0.328	(a)	.0.5	535	0.539		
	Agitation (hours)	Bitumen Sep'd	Agitation (hours)	Bitumen Sep'd	Agitation (hours)	Bitumen Sep ⁱ d	
First Agitation	15.3	0 . 249(b)	19.5	0.334	36•5	0.210	
Second Agitatio	n 13 . 2	0.211	21.2	0.311		in - in	
Total	28.5	0.460	40.7	0.645	36.5	0.210	

(a) Weight fraction of the total system.

(b) Meight fraction of the total bitumen in the system.

TABLE XIII

THE SEPARATION OF BITUMEN AS PLASTIC PHASE

FROM THE RESTRICTED PENTANE-TETRALIN-BITUMEN SYSTEM

Temperature (deg F)	Pentane Weight Fraction	AT 8000 PSIA Distribution Plastic Phase	of the Bit Liquid Phase I	umen Liquid Phase II
70	0.328 (a)	0.458 (b)	0.489 (b)	0.153 (b)
70	0.535	0.645	0.355	0.000
70	0.539	0.210	0.000	0.860
160	0•434	0.429	0•394	0.177
160	0•558	0.111	0•000	0.914
160	0•606	0.416	0•139	0.445
220	0.442	0•487	0•513	0.000 (c)
220	0.640	0•640	0•360	0.000 (c)

(a) Weight fraction of pentane in the system.

(b) Weight fraction of the total bitumen in the system.

(c) Liquid phase II was not obtained at this state.

TABLE XIV

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THE SEPARATION OF BITUMEN AS PLASTIC PHASE FROM THE

RESTRICTED DECANE-TETRALIN-BITUMEN SYSTEM AT 8000 PSI ABSCLUTE

Compos	ition of S	System		Distribut	ion of th	e Bitumen
Decane	Tetralin	Bitumen		Plastic Phase	Liquid Phase I	Liquid Phase II
			70 Deg F			
0.430 (a) 0.607	0•542 0•373	0.0285 0.0196	2	0.355 (b) 0.134	0•568 0•376	0.077 0.490
			160 Deg F			
0 .412 0 . 589	0•559 0•390	0.0294 0.0206		0.408 0.310	0.359 0.160	0•233 0•530
			220 Deg F			
0.425 0.654	0.546 0.329	0.0288 0.0173		0.623 0.717	0.201	0.176 0.221
(a) Weig	tht fractio	on of the	total syste	em •		

(b) Weight fraction of the total bitumen in the system.

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TABLE XV

A COMPARISON OF THE GRAVIMETRIC AND REFRACTOMETRIC METHODS

FOR DETERMINING THE COMPOSITION OF THE LIQUID PHASE (a)

Component	Gravimetric	Refractometric
Methane (b)	0.131 (d)	0.132
Decane	0.067	0.064
Tetralin	0.781	0.785
Bitumen	0.022	0.018
Methane (c)	0.130	0.135
Decane	0.073	0.076
Tetralin	0.784	0.777
Bitumen	0.013	0.013

- (a) Prepared by C. Yundt.
- (b) Composition of system corresponds to 0.442 weight fraction methane. See Table XVII.
- (c) Composition of system corresponds to 0.283 weight fraction methane. See Table XVII.
- (d) Composition expressed as weight fraction.

TABLE XVI

ULTIMATE AMALYSIS OF THE TWO BITUMEN PREPARATIONS

Sample	Carbon	Hydrogen	™itrogen	Sulfur	Ash	Mercury	C/H Ratio
Refined Bitumen Sample 1	0.8417 a	0.0716	0.0080	¢ 0•0122	0.0097	7	11.76
Refined Bitumen Sample 2	0.8494	0.0752	0.0061	0.0227	0.0136	5 0 . 0041	11.30

(a) Composition expressed as weight fraction.

TABLE XVII

CHARACTERISTICS OF THE RESTRICTED METHANE-DECANE-

TETRALIN-BITUMEN SYSTEM AT 8000 PSIA AND 220 DEG F.

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Wt. Fraction	tion Wt. Fraction Weight Fraction of Phases in System				Compositions of the PHases ^c						
in Grate	Bicumen Generated	0-1-1-1	•••			Gas Phase		14	Liquid	Phase	
In System .	Separated	Solid	Liquid	Gas	Methane	Decane	T e tralin	Methane	Decane	Tetralin	Bitumen
0.211ª	0.027	0.0010									
0.350	0.140	0.0042									
0.493	0.399	0.0093			ж ^с						
0.550	0.099	0.0020				·					
0:663	0.137	0.0021									
0.737	0.459	0.0060	0.113	0.881	0.835	0.021	0.144	0:013	0.040	0 876	0.062
0.842	1.000	0.0078	0.041	0.951	0.885	0.009	0.106	0.01)	0.049	0.010	0.002
0.949	1.000	0.0028			0.00)	0.007	0.100	./			
1					0.581	0.088	0.331	0.113	0.077	0.780	0.029
0 .1 47 ^b	0.299	0.0114	0.914	0.074	0.737	0.048	.0.215	0.130	0.073	0.784	0.013
0.283	0.727	0.0239	0.720	0.256	0.750	0.043	0.207	0.113	0.065	0.806	0.016
0.403	0.685	0.0183	0.522	0.459	0.766	0.036	0.198	0.131	0.067	0.781	0.022
0.442	0.585	0.0150	0.493	0.492	0.827	0.033	0.140	0.094	0.065	0.794	0.048
0.466	0.101	0.0026	0.489	0.508	0.839	0.031	0.130	0.088	0.063	0.793	0.056
0.500	0.021	0.0005	0.451	0.549	0.771	0.036	0.193	0.096	0.052	0.796	0.056
0.544	0.073	0.0015	0.336	0.663	0.821	0.033	0.145	0.078	0.044	0.811	0.068
0.598	0.022	0.0005	0.299	0.700	0.835	0.024	0.141	0.068	0.043	0.809	0.082
0.703	0.097	0.0014	0.171	0.828	0.852	0.017	0.132	0.053	0.051	0.796	1.000
0.791	0.329	0.0036	0.073	0.924	·			//			

(a) Prepared from bitumen sample 1.

(b) Prepared from bitumen sample 2.

(c) All phase compositions are expressed as weight fractions.

TABLE XVIII

THE EQUILIBRIUM CONSTANTS AND THE SOLUBILITY OF BITUMEN FOR A RESTRICTED METHANE-DECAME-TETRALIN-BITUMEN SYSTEM AS A FUNCTION OF THE MEAN MOLECULAR WEIGHT OF THE LIQUID

PHASE (a)

Average Molecular	Weight Fraction				
Weight of	Methane				Solubility
the Liquid	in the	Equilib	rium Constan	nts for	Ratio for
Phase	Liquid	Methane	Decane	Tetralin	Bitumen (b)
103.2	0.0529	2.88	0.05	0.03	0.0594
94.2	0.0675	2.47	0.11	0.03	0.0726
88.2	0.0776	2.28	0.15	0.04	0.0884
81.5	0.0937	2.03	0.12	0.06	0.1100
81.0	0.0961	1.99	0.17	0.06	0.0220
73.6	0.1129	1.86	0.17	0.07	0.0127
68.6	0.1304	1.72	0.20	0.08	0.0164
68.8	0.1309	1.72	0.15	0.07	0.0301
			-		

(a) Restricted to decane: tetralin: bitumen = 2:19:1 and conditionsof 8000 psia and 220 deg F.

(b) Solubility ratio expressed as grams of bitumen in solution per gram of volatile material.

TABLE XIX

THE SEPARATION OF BITUMEN FROM THE RESTRICTED METHANE-DECANE-TETRALLY-BITUMEN SYSTEM AT 8000 PSIA AND 70 DEG F. (a)

Concentration of Methane	Bitumen Separated as Solid Phase	Bitumen in Second Liquid Phase
0.108 (b)	0.017 (c)	0.983 (c)
0.173	0.545	0.455
0.245	0.211	0.020 (d)
0.295	0.272	0.728 (e)

- (a) Restriction -- Decane: tetralin: bitumen = 2:19:1.
- (b) Weight fraction of the system.
- (c) Weight fraction of the total bitumen in the system.
- (d) A second liquid phase containing 0.769 weight fraction of the total bitumen in the system was obtained at this methane concentration.
- (e) Although a second liquid phase was not observed at this methane concentration, it may have been present since the detection of the second liquid phase is difficult in this system due to the large volatile content at appreciable methane concentrations.