PHASE BEHAVIOR IN PETROLEUM FLUIDS: A DETAILED DESCRIPTIVE AND ILLUSTRATIVE ACCOUNT WITH EMPHASIS ON HEAVY ORGANICS

G. Ali Mansoori
Departments of BioEngineering, Chemical Engineering & Physics, University of Illinois at Chicago, Chicago, IL 60607-7052 USA

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Contents

Summary

This chapter presents a descriptive and illustrative account of phase behavior in the seven naturally occurring petroleum fluids and ties all the known eleven phase-transition concepts in a unified narrative. The figures and tables contained in this report are designed so that they could effectively support the discussion about molecular make-up of petroleum fluids, P- and T-effects on phase behavior and phase transition points.

Seven naturally occurring hydrocarbon fluids are known as petroleum fluids. They

include, in the order of their fluidity, natural gas, gas-condensate (NGL), light crude, intermediate crude, heavy oil, tar sand and oil shale. In this report we present a generalized description of the various phase transitions, which may occur in petroleum fluids with emphasis on heavy organics deposition.

At first the nature of every petroleum fluid is presented. Their constituents including their so-called impurities are identified and categorized. Heavy fractions in petroleum fluids are discussed and their main families of constituents are presented including petroleum wax, diamondoids, asphaltenes and petroleum resins.

Then the generalized petroleum fluids phase behavior is discussed in light of the known theory of phase transitions. The effects of variations of composition, temperature and pressure on the phase behavior of petroleum fluids are introduced.

Finally eleven distinct phase-transition points of petroleum fluids are presented and their relation with state variables and constituents of petroleum fluids are identified. This report is to generalize and relate phase behaviors of all the seven naturally occurring petroleum fluids into a unified perspective. This work is the basis to develop a comprehensive computational model for phase behavior prediction of all the petroleum fluids, which is of major interest in the petroleum industry.

1. Introduction

The petroleum and natural gas literature is quite rich in data, industrial correlations and molecular-based prediction methods of the liquid-vapor phase behavior of petroleum fluids (see [1]-[17]). For this reason little effort is made to discuss further liquid-vapor equilibrium in this report. Our emphasis is to introduce a generalized perspective about all the variety of phase transitions, which may occur in the seven category of naturally occurring petroleum fluids. This includes vapor separation, solid crystalline deposition, colloidal and micellar solutions formation as well as aggregation, flocculation and non-crystalline solid formation and separation.

We are in the process of developing a comprehensive phase behavior prediction package for petroleum fluids, which can be applied to any of the seven categories of such fluids from underground natural reservoirs. Having a thorough understanding of all the possible phase transitions in the seven categories of petroleum fluids will allow us to formulate the necessary computational package for their phase behavior prediction regardless of the kind, source, nature of components and thermodynamic conditions.

1.1. Naturally Occurring Petroleum Fluids

There exist seven well-known petroleum fluids in nature. In the order of their fluidity, they are natural gas, gas-condensate (also known as NGL standing for natural-gas liquid), light crude, intermediate crude, heavy oil, tar sand and oil shale as shown symbolically in Figure 1. These are all naturally occurring complex mixtures made up of hydrocarbons and other organic and inorganic compounds with variety of molecular structures and sizes.

Figure 1. The normal conditions of the seven naturally occurring petroleum fluids, in the order of fluidity from left to right, natural gas, gas-condensate (NGL), light crude oil, intermediate crude oil, heavy oil, tar sand and oil shale.

The hydrocarbons and most other organic compounds present in all these seven naturally occurring petroleum fluids are generally polydispersed having a range of size, shape and molecular weight distributions (see for example [18]). As a result continuous functions may be used for their mole fraction distributions (see for example [19-24]). In Figure 2 we report the approximate relative composition of various petroleum fluids with respect to the number of carbon atoms of their organic contents.

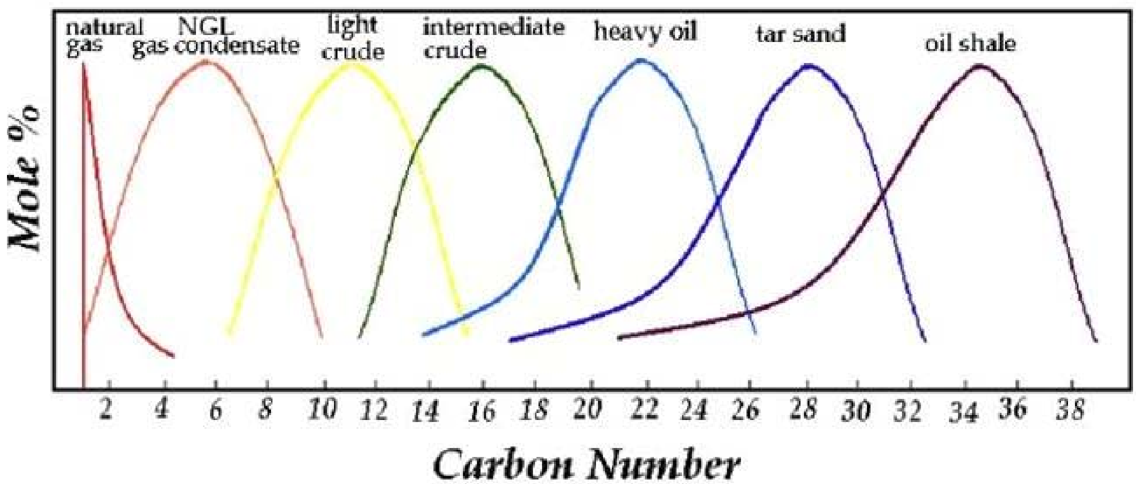

Figure 2. Various categories of natural gas and liquid hydrocarbon reserves and their approximate hydrocarbon molecular weight distributions according to their carbon numbers

We think this is a useful way to classify petroleum fluids according to their composition. This novel classification will allow us to look at all the petroleum fluids from a unified basis which is their hydrocarbon contents and their relative distribution. According to this figure, the molecular weight of hydrocarbons present in petroleum fluids increases from left to right in the list of the seven. It should be also mentioned that heavy oil, tar sand and oil shale contain appreciable amounts of resins and asphaltenes, while the percentages of these compounds are generally low in the lighter petroleum fluids.

Petroleum fluids vary in color, odor, and physicochemical properties. Generally many compounds are known to be present in petroleum fluids. The number of carbon atoms in the hydrocarbons and other organic compounds present in petroleum fluids can vary from one (as in methane) to over a hundred (as in asphaltenes and heavy paraffins) [25, 26].

During their production, transportation and processing petroleum fluids may go through a number of phase changes, which include evaporation (separation of gases from liquid streams), retrograde condensation (separation of liquids from gas streams) and solids formation and deposition (separation of crystalline solids, colloids and aggregates from liquid or vapor streams). The latter is mostly due to precipitation and / or deposition of diamondoids, wax and asphaltenes. In view of the complexity of petroleum fluids, study and understanding of their phase behavior is still a challenging and an industrially important task. Such an understanding will help us to design a more economical route for the related production, transportation and refining projects. The complexity of the phase behavior in petroleum fluids is due to the existence of the variety and polydispersity of hydrocarbons and other organic molecules in them. In this report, we present the various phase-transitions, which may occur in petroleum fluids, and we introduce a unified perspective of their phase behaviors. This may allow us to develop a comprehensive theoretical model for phase behavior prediction of all the petroleum fluids which is of major concern in the petroleum industry.

2. Components of Petroleum Fluids

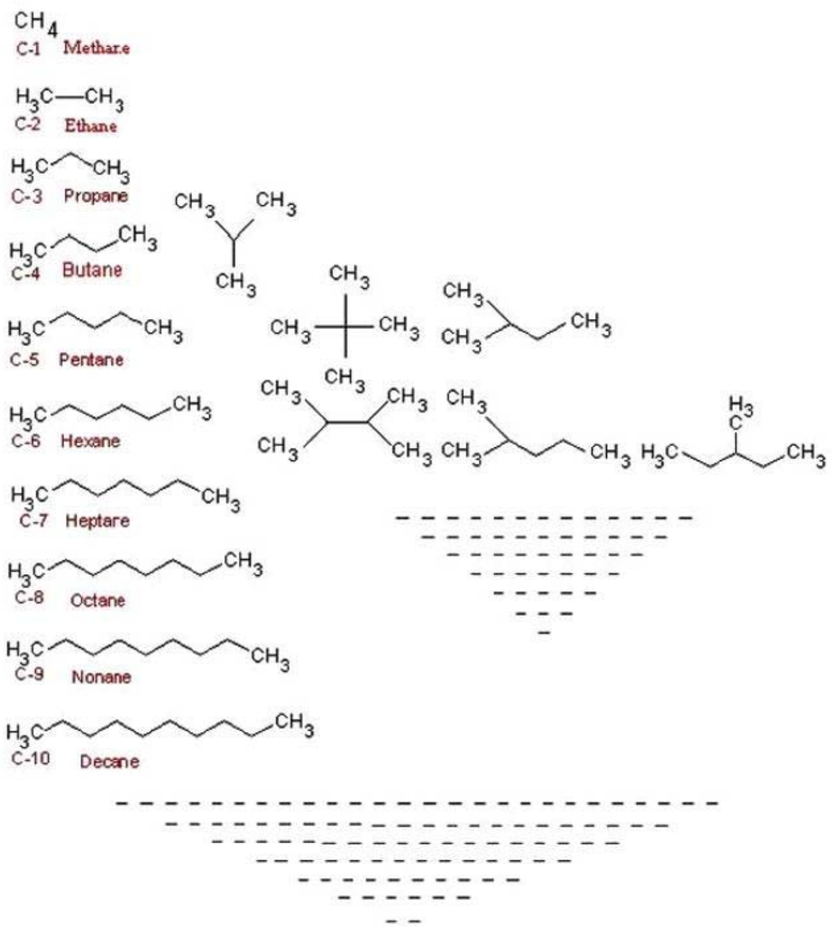

Figure 3. Lighter paraffin hydrocarbons present in petroleum fluids

The predominant hydrocarbons present in lighter petroleum fluids (natural gas, gas-condensate, light-crude and intermediate-crude oil systems) are alkanes (also known as paraffin hydrocarbons) as shown in Figure 3.

As we look at the physical properties of petroleum fluids, going from natural gas to oil shale, their alkanes content decrease while their viscosity and density increase. Other hydrocarbons present in petroleum fluids are aromatic hydrocarbons (see Figure 4) at somehow lower concentrations than paraffins depending on the underground natural reservoir source. Other families of hydrocarbons are also present in petroleum fluids but their concentrations are generally rather low.

Quite frequently, petroleum fluids contain various amounts of other organic and inorganic compounds, which are usually termed as impurities from the petroleum industry point of view.

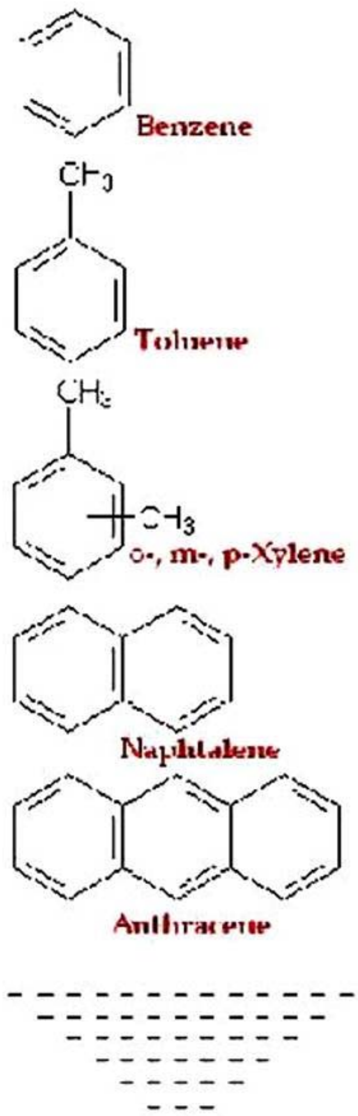

Figure 4. Lighter aromatic hydrocarbons present in petroleum fluids

2.2. Impurities in Petroleum Fluids

All the non-hydrocarbon organic and inorganic components of petroleum fluids are considered impurities from the petroleum industry perspective. Molecular structure of organic impurities is composed of mostly such elements as carbon, hydrogen, metals, nitrogen, oxygen and sulfur. Molecules of inorganic impurities are generally composed of carbon, metals, oxygen and sulfur. Petroleum fluid impurities can be categorized into five groups of compounds:

(i) The major low molecular weight impurities, which include carbon dioxide (CO_2), hydrogen sulfide (H_2S), metal oxides (Al_2O_3, Fe_2O_3, SiO_2, etc.), nitrogen (N_2), oxygen (O_2), salts (NaCl, $CaCO_3$, etc.), sulfur (S) and water (H_2O).

(ii) High molecular weight impurities, which could be present in the petroleum fluids heavy fractions. They include asphaltenes, asphaltogenic acids, diamondoids and derivatives, mercaptans, metal carbenes, organometallics, petroleum resins and wax. In Table I the general closed chemical formulae of high molecular weight impurities of petroleum fluids are presented.

(iii) There may be also other organic and inorganic compounds present in petroleum fluids, which depend on their underground natural reservoir source. The concentration of such other organic matter is generally rather low and they have little or no effect on petroleum fluids phase behavior.

(iv) Another category of impurities which may be present are compounds which have been added to petroleum fluids during their production, transportations and storage stages for various reasons. These include but not limited to acids, alcohols, aromatic hydrocarbons, detergents and polymers.

(v) Petroleum fluids often contain compounds, which are a result of physical association of hydrocarbons and the above-mentioned impurities and contaminants. They include clatherates, colloids, crystalline solids, flocs and slugs.

High Mw Impurity	**General Closed Formula**
Asphaltenes	$C_mH_nN_iO_jS_k$
Asphaltogenic Acids	$C_mH_nN_iO_jS_k$-COOH
Diamondoids	$C_{4n+6}\ H_{4n+12}$
Mercaptans	$C_mH_nN_iO_jS_kX$
Metal Carbenes	$R_1HC{=}CHR_2X$
Organometallics	*Ex.:* R_1-X-R_2
Petroleum Resins	$C_mH_nN_iO_jS_k$ i,j,k=0 or 1
Wax	C_mH_n $18 \le m \le 60$ $n \le 2m+2$

Table 1: General closed chemical formulae of high molecular weight impurities of petroleum fluids. In this table C is carbon, H is hydrogen, N is nitrogen, O is oxygen, S is sulfur and X is metals and R represents a hydrocarbon segment.

As it was mentioned above the literature on petroleum and natural gas is rich of numerous data banks, correlations, and nomograms for the analysis and treatment of petroleum fluids and their liquid-vapor phase behavior.

The presentation given in this report is an attempt to relate properties and phase behavior of petroleum fluid systems to the molecular behavior of the compounds present in them. This would allow us to make a unified and a science-based generalization of the behavior of petroleum fluids.

One of the important fractions of petroleum fluids, which is the least understood is their heavy fraction. Because of the complexity of the heavy fractions, we discuss them in more detail in the following separate section.

2.3. Heavy Fractions in Petroleum Fluids

To perform an accurate prediction of the phase behavior of petroleum fluids we need to know the nature and composition of the molecules, which make up the petroleum heavy fractions [27]. There is a wealth of information and database available for the light and intermediate components of petroleum fluids [1-17].

The investigation of the accurate chemical constitution of petroleum heavy fractions is hindered by their complex nature. Almost all the molecules comprising the heavy fractions of petroleum fluids are polydispersed [18, 27, 28, 29].

The predominant part of the high molecular weight impurities (known as heavy fractions or petroleum residuum) are asphaltenes, asphaltogenic acids/compounds, diamondoids and derivative, heavy aromatic hydrocarbons, mercaptans, metal carbenes / organometallic, petroleum resins and wax. In Table 1 we report the general closed chemical formulae of these compounds.

It is generally understood that heavy fractions have little or no effect on the liquid-vapor phase behavior of the majority of petroleum fluids. Their main contribution is in the solids separation from petroleum fluids, due to changes in the composition, temperature and pressure.

The main components of the heavy fraction, which participate in the solid phase formation, include asphaltenes, diamondoids, petroleum resins and wax. In what follows we present a more detailed description of their molecular characteristics and their physical properties.

2.3.1. Petroleum Wax

Petroleum wax is a class of mineral wax that is naturally occurring in the heavy fractions of petroleum fluids [30-37]. They vary compositionally over a wide range of molecular weights up to hydrocarbon chain lengths of approximately C_{60} [34]. Petroleum wax is made up mostly of saturated paraffin hydrocarbons with their number of carbon atoms in between 18-36 (see Figure 5).

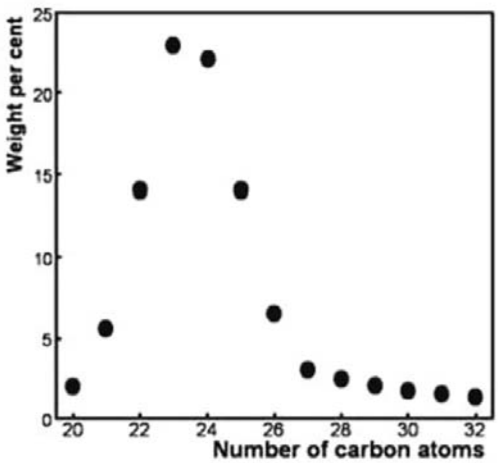

Figure 5.The distribution of n-alkanes in Suntech P116paraffin wax as a function of the number of carbon-atoms (Taken from [32])

Wax may also contain small amounts of naphthenic hydrocarbons with their number of carbon atoms in the range of 30-60. Wax usually exists in intermediate crudes, heavy oils, tar sands and oil shales. Petroleum wax is typically in solid state at room temperature and it is separated from relatively high boiling petroleum fractions during the refining processes. Petroleum wax, like most other components of heavy end of petroleum fluids, is polydispersed. As an example, we report in Figure 5 the distribution of n-alkanes as a function of the number of carbon-atom compounds in a paraffin wax sample.

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Biographical Sketch

G.Ali Mansoori received BSc-*ChE* degree from University of Tehran, MSc-*ChE* degree from University of Minnesota, PhD from the University of Oklahoma and his postdoctoral training at Rice University, the latter in 1970. He is a professor of bioengineering, chemical engineering and physics at the University of Illinois at Chicago. He has been a visiting professor at University of Pisa, ITB, University of Kashan, Sharif University of Technology; and a visiting scientist at the Argonne National Laboratory, National Institute of Standards and Technology and CNR-Pisa. He has been a consultant to ARCO, BJ Services, British Petroleum (BP), C3 Int'l-LLC, Chevron Oil Field Services, DuPont, Exxon, Eng. Research Corp., Federation of American Scientists, Harza Eng. Co., Hitachi, Ltd., Hydrotech, IMP, Institute of Catalysis of Novosibirsk-Russia, Mitsubishi Chemicals, Motorola, MUCIA, NIGC, NIOC, Norsk Hydro, PEMEX, PETROBRAS, PetroStat Laboratories, Science Applications., Shell Int'l B.V., Synethic/Johnson-Matthey, Technology International., The Anián Community (Reuters), United Nations (UNDP; TOKTEN Project), UOP-LLC, Vista Research. Dr. Mansoori's academic and professional honors include: Academician of the International Academy of Creative Endeavors (science, arts, social issues); Algorithm scientific international award; diploma of honor from Pi Epsilon Tau National Petroleum Engineering Honor Society; honorary academician of the International Eco Energy Academy; Kapitsa gold medal from the Russian Academy of Natural Sciences; medal of fundamental science from UNESCO; recognition of dedicated service award from the fuels & petrochemicals division of AIChE, science medal from *Vezarat a Farhang va Aamozesh Aali*, honorary member of the IRI National Academy of Sciences, undergraduate instructional award from UIC. His research and educational activities include arterial blockage / fouling in petroleum and natural gas industries, atomic and molecular nanotechnology, molecular based study of condensed matter, disease diagnostic methods and therapeutic agents, nanostructures design (nanoclusters, nanoconjugates, nanoparticles), phase transitions, *ab initio* methods, density functional and molecular dynamics simulations, statistical mechanics, thermodynamics. Prof. Mansoori has published over 350 technical papers including seven books.