Toward Common Generalized Phase Diagrams for Asphaltene Containing Hydrocarbon Fluids

John M. Shaw

Professor and NSERC Industrial Research Chair in Petroleum Thermodynamics
Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, T6G 2G6, Canada
Telephone: 780-492-8236 - Fax: 780-492-4534
E-mail: jmshaw@ualberta.ca

Introduction

Many hydrocarbon liquids of industrial interest from reservoir fluids to bitumen + diluent mixtures share constituents, from asphaltenes and resins to pentane, and can be classified as asymmetric from a phase behavior perspective. The phase diagrams for these asymmetric fluids are characterized by lenses of four-phase behavior surrounded by three and two regions in both P-x at constant T, and P-T at constant x diagrams. Interest in the phase behavior of reservoir fluids focuses on understanding the impact of phase behavior on flow assurance, risk assessment and other reservoir fluid management issues at temperatures ranging form 270 K to 470 K and pressures ranging from atmospheric to ~ 100 MPa. Until recently, the focus within the heavy oil and bitumen extraction and upgrading sector has been at temperatures greater than 650 K and at pressures ranging from atmospheric to 20 MPa where catalyst coking, line plugging and other refining issues are key applications. Renewed interest in the development of pre-processes for the selective elimination of mineral matter and other undesirable constituents from heavy oil has heightened interest in ROSE like separation processes which have operating conditions and compositions overlapping with those arising in reservoir fluids. Despite this overlap the two literatures remain disparate. Much can be gained by combining achievements from both sectors particularly with respect to the asphaltene deposition issue, a hot topic for both sectors. Qualitative four component phase diagrams can be used to illustrate key features present in the phase diagrams for the entire range of fluids and can provide a sound basis for detailed mathematical model development. This concept will be introduced and discussed using examples drawn from both the reservoir fluids and bitumen + diluent mixtures.

Phase Behavior of Asymmetric Mixtures

Model and actual reservoir fluids have both been shown to exhibit multiphase equilibria in and of themselves or on addition of other fluids. In particular, the addition of carbon dioxide, nitrogen, and light hydrocarbon gases to reservoir fluids as envisaged in a number of secondary recovery process schemes is known to induce or enhance such complex phase behaviour over the range of pressures and temperatures encountered in hydrocarbon reservoirs. For example, Shelton and Yarborough found that the addition of carbon dioxide or a more or less equimolar mixture of methane, ethane and propane to a condensate rich reservoir fluid yielded four organic phase zones (solid-liquid-liquid-vapour) at intermediate pressures as well as large three phase (solid-liquid-liquid and solid-liquid-vapour) zones. Solids drop out can also occur during normal reservoir depletion.

Valuable hydrocarbons distributed among these various condensed phases or trapped by solid plugs is difficult to recover and treat, and consequently the utility of recovery processes, for example, based on the injection of driving gases is limited when complex phase equilibria arise. Thus there are incentives to have accurate phase diagrams and to be able to predict or interpolate phase behaviour. The appearance, prediction and properties of liquid-liquid-vapour and solid-liquid-liquid-vapour regions in model reservoir fluids has been addressed previously. This qualitative and mechanistic understanding can be applied to the development of phase diagrams for systems of practical interest. However, it is important to recognize that the reversibility of phase behavior of some components particularly asphaltenes remains a subject of some debate.

Similar observations of multiphase behavior have been made with heavy oils and bitumen + diluent and related model systems.

Phase Diagram Construction for Reservoir Fluids and Heavy Oils

Composition Variables. Reservoir fluid and heavy oil compositions are frequently reported in terms of saturates, aromatics, resins, asphaltenes (SARA), and light hydrocarbons and gases (C1-C7, H2S, etc.) if present. Occasionally, more detailed structural information is available. However, from the perspective of phase diagram construction even these composition variables + pressure and temperature pose a complex challenge and further lumping is frequently justified. The two literatures diverge on how the lumping should be performed. For reservoir fluids, the typical scheme is to treat saturates + aromatics + resins as a single fraction, “oil” or more correctly maltenes, which permits one to construct ternary diagrams using the pseudo components light gases, maltenes and asphaltenes at fixed temperature and pressure. For bitumen and heavy oil systems, the light components are typically ignored and one encounters pseudo binary and more typically ternary diagrams where the composition variables are asphaltenes, and one or two oil fractions. Thus the impact of the variability of the phase behavior of the high molar mass constituents on the phase behavior of reservoir fluids is largely ignored in one literature and the impact of low molar mass constituents on the phase behavior of heavy feed stocks is largely ignored in the other. As a consequence, the phase behavior of individual fluids is treated as unique and must therefore be addressed primarily from an experimental perspective. Mathematical extrapolation of correlated phase behavior in pressure, temperature, and composition has met with very limited success. The challenge one faces in re-unifying the two literatures is illustrated in Figure 1. It comprises a four pseudo-component phase diagram and shows how typical reservoir fluid and heavy oil phase diagrams intersect at fixed temperature and pressure. The line of intersection is unknown and comprises two random variables (the position along the oil I - oil II, dictated by the maltenes composition of the reservoir fluid, and the elevation of the
heavy oil phase diagram within the pyramid dictated by the light hydrocarbon fraction of the heavy oil) that render the two phase-diagram topologies incompatible. Clearly, a minimum of four pseudo components must be considered and equally clearly the same set of pseudo components must be considered for both reservoir fluids and heavy oils. From a thermodynamic perspective, four component mixtures are the simplest mixtures that exhibit four-phase behavior over ranges of temperature, pressure and composition.

The Phase Behavior of the Pseudo Components. The pseudo components comprise the apexes of the pyramid. There are four in total. One must determine the phase behaviour of each of the pseudo components at the temperature and pressure of interest. For example, one must determine whether the light component mixture is a liquid, vapour, liquid + vapour, or supercritical fluid under the conditions of interest. The phase behaviour of well defined fluids particularly the low molar mass hydrocarbons is well understood and can be modelled accurately using standard techniques implemented in a variety of commercial and proprietary software packages (c.f.: Okazawa et al.\textsuperscript{21}). The oil I and oil II pseudo components chosen on the basis of boiling range or structure, can normally be considered to be a liquid phase, although if the temperature is low enough solid + liquid phase behavior can be anticipated. The bulk phase behavior of asphaltenes, regardless of how they are defined, can normally be considered to be a solid or solid + liquid mixture. A recent paper by Yarranton and Masliyah\textsuperscript{12} presents an excellent introduction to the relevant literature on asphaltenes their properties and composition.

The Phase Behaviour of the Pseudo Binaries. Pseudo binary mixtures comprise the axes of the pyramid. There are six in total. The phase behavior of binary organic fluids has been classified by Van Konynenburg and Scott.\textsuperscript{13} They identified six basic types of fluid phase behavior but did not consider the formation of solid phases that arise, in all cases, if the triple point of the heavier component is high enough. Peters et al.\textsuperscript{13} show how solid can be included in binary phase diagrams and provide an example for a type V binary fluid. Additional examples can be found elsewhere.\textsuperscript{24} Many binary organic fluids also exhibit liquid-liquid-vapour phase behavior.\textsuperscript{7,14} Again, if the triple point of the heavier component is high enough, solid formation interferes with the liquid-liquid-vapour curve and it terminates at a four phase point, a so-called quadruple-point or q-point, where four organic phases are present: solid (S), light liquid (L\textsubscript{1}), heavy liquid (L\textsubscript{2}), and vapour (V). Binary fluids such as propane + phenanthrene or fluorene exhibit this type of phase behaviour. For the propane + phenanthrene example, the solid is essentially pure phenanthrene, the gas is essentially pure propane, the light liquid is more than 95 mole % propane, the heavy liquid is about 60 mole % phenanthrene. As more degrees of freedom are available for more complex mixtures, the four-phase point expands to a curve for three component mixtures and becomes a region for mixtures with four or more components. Thus the pseudo binary pairs that form the axes of the diagram can easily exhibit up to four phases in equilibrium. As three and four phase zones are bounded by specific sequences of other multiphase zones such features can provide a wealth of information about the phase behaviour of the interior of the phase diagram and allow one to anchor experimental observations with greater confidence.

The Phase Behavior of Pseudo Ternaries and Quaternaries. Remote from the axes there are no restrictions imposed on phase behaviour and other multiphase zones and related critical phenomena can arise.\textsuperscript{25} This highlights the need for coordinated research activities to which help define the phase behavior of the four pseudo ternary mixtures present in the general phase diagram as well as the need to report all relevant composition data. All to frequently, in the heavy oil/bitumen literature, for example, the pressure of gases and not their mass or mole fraction are reported.

Illustrative Example. To underscore the complexity of the task let us consider a pseudo ternary case, i.e.: the preparation of a phase diagram consistent with the data of Werner et al.\textsuperscript{4} who examined the phase behavior of model reservoir fluids that contained mixtures of methane + propane in the mole ratio 1:5, and pure CO₂ as the “gas” component. The balance of the fluids comprised linear and cyclic hydrocarbons and two vacuum residus from the Athabasca basin. The authors observed the phase behavior of eight separate mixtures at 373 K and 35 MPa. Six samples exhibited solid + a low-density liquid phase behavior; one exhibited solid + liquid + liquid phase behavior; one exhibited dense liquid phase behavior. They then filtered out any solid present and reported the density, composition and viscosity of the single-phase fluid retained at elevated temperature and pressure thus providing information about the phase boundaries and the nature of the phases present. Such a data set is typical in that the data are sparse. The key from the perspective of generating a phase diagram is the quality of the observations and the phase density and viscosity measurements. For details concerning their experimental methods and findings the reader is referred to their paper.

As the critical temperatures of the light hydrocarbons in question are well below 373 K, the gas component is a vapor.
regardless of the pressure. The maltene pseudo component is largely a mixture of C8 to C18 compounds of various structures that are assumed miscible under these conditions. Asphaltenes due to their solubility based definition at ambient temperature and pressure can be treated as a solid or a solid + liquid mixture without altering the general structure of the phase diagram. At the temperature in question, asphaltenes are treated as a solid + liquid mixture. From the work of Cartlidge et al.,19,20 a L to SL transition is expected along the maltene-asphaltenes axis at ~ 40 wt % asphaltenes. More recent experiments,24 Figure 2, suggest that the maltene-asphaltenes axis is potentially even more complex. As asphaltenes by definition are insoluble in pentane etc., the gas or light hydrocarbon - asphaltene axis is dominated by gas, gas-liquid-solid and liquid-solid zones.

The light hydrocarbon - maltene axes presents a more complex situation. At 373 K binary mixtures of propane + straight chain hydrocarbons exhibit L1L2 and L1L2V phase behavior for carbon numbers 32 to 40 and SL1L2V phase behavior does not arise for up to at least n-C40.13 With the addition of methane such behavior is shifted to significantly lower temperatures19 although the range of carbon numbers affected is broadened. Methane + n-C24 and related binaries tend to exhibit SLV phase behavior at temperatures at or slightly below the triple point temperature of the heavy hydrocarbon. Thus L, LV, V phase behavior is expected up to at least n-C40 - at 373 K. Propane + phenanthrene13 and propane + phenanthrene + ethane + butane mixtures2 both exhibit L1L2 phase behavior up to ~ 18 MPa at 373 K. For the propane + phenanthrene binary the liquid-liquid critical point is at a composition of 70 mole % or 37 wt % propane. For methane + phenanthrene at 373 K and 35 MPa, V and LV phase behavior is observed as this condition is above the triple point of phenanthrene and below the SLV curve of the phenanthrene-methane binary. At higher pressures V, SF, SLV phase behavior is observed because the SL=V critical point is at 403 K and 360 MPa.24 Complex phase behavior arises along or near the gas-maltene axis as a consequence of gas + polynuclear aromatic constituents in the maltenes, where the carbon number of the heavy hydrocarbon is ~ 14 or greater. Thus L1L2 and SL1L2 or incipient phase behavior of this sort is anticipated for the mixtures of Werner et al.1 under these conditions as the C14 + aromatic fractions for the fluids tested are in the range 9 to 24 wt %. Solids present could include polynuclear aromatic compounds as well as asphaltenes. From the data of Floter et al.24 the L1V to V boundary along the gas oil axis is likely to be in the range of 0.5 mole % or 2 wt. % maltenes. Propane, methane and carbon dioxide are quite soluble in heavy hydrocarbons and consequently the L1V to L1 phase boundary is in the order of 50 wt. % maltenes.

Thus one anticipates L1L2 phase behavior and SL1L2 phase behavior at or near the gas-oil axis to arise as a consequence methane or propane + polynuclear aromatic hydrocarbon interactions. Three possible resulting phase diagrams are shown as Figures 3 a, b & c respectively. Due to the low solubility of asphaltenes in light solvents the L1, L1V, L1L2 and V regions are expected to be small and to arise close to the gas-oil axis. SV and SL2 regions and an SL2V region fall along the gas-asphaltene axis, as the gas is well above its critical point at the temperature in question. In addition, a SL1L2V four phase region arises within the diagram as a consequence of the other multiphase regions present and the proximity of the observed SL1L2 phase behavior to the anticipated L1V region. As drawn the SL1L2V region extends across to the gas - asphaltene axis. This need not be the case as the SL2V and SV regions can also share a boundary.

By placing the data of Werner et al.6 in this framework, one can sketch the basic form of the phase diagram for the system studied and provide semi-quantitative phase boundaries as noted in Figure 4. The phase boundaries are approximate but respect their phase behavior observations as well as their liquid viscosity and density data. Dashed lines are used where the boundaries are uncertain. The L1 - L1S boundary was constructed from the de-asphalted samples exhibiting SL1 phase behavior. The SL1 - SL1L2 boundary was approximated from the sample exhibiting SL1L2 phase behavior and the samples exhibiting SL1 phase behavior. The slope of the boundary is well constrained by these data. The point of intersection of these two boundaries is also a point on the SL1L2 - L1L2 and L1 - L1L2 phase boundaries. From plots of viscosity, gas and asphaltene content of the homogeneous liquid phases L1 and L2 vs. density, a L1=L2 critical point was identified at a liquid density of approximately 730 kg/m³, with a gas content between 10 and 20 wt% and an asphaltene content in the 1 to 3 wt % range. The critical point indicated in the phase diagram is therefore approximate. The L1L2 - L2
The phase boundary is drawn parallel to the SL1L2 - SL1 phase boundary and its location is tentative as there is only one L2 phase behavior datum available. However, the L1=L2 critical point is typically at an extremum of the L1L2 phase behavior so the placement of the boundary is not likely to be far off the mark. The other phase boundaries are speculative as noted above but are constrained by the data available in the literature concerning the axes.

**Figure 3.** Sketches of the anticipated phase diagrams for oil + gas + asphaltene systems at 373 K and 35 MPa based on the phase behavior along the axes: a) gas + oil mixtures exhibit only V, LV and L phase behavior, b) gas + oil mixtures exhibit V, L1V, L1, L1L2 and L2 phase behavior, c) gas + oil mixtures exhibit V, L1V, SL1, SL1L2, L1L2 and L2 phase behavior.

**Figure 4.** A scaled drawing of a phase diagram for gas + oil + asphaltene mixtures at 373 K and 35 MPa based on the data of Werner et al. Clearly, the data reported by Werner et al. most closely resemble the phase diagram depicted in Figure 1a. Key features of the diagram include the low density liquid region, the L1 region, which falls in a narrow band along the gas-oil axis where the asphaltene content is less than 0.3 wt %, and the more dense liquid region, the L2 region, which occupies a much more substantial part of the phase diagram. These two homogeneous regions are separated by a sequence of multiphase regions at intermediate asphaltene concentrations that reflect the transition from a “light liquid” saturated with heavy constituents to a “heavy liquid” saturated with lighter constituents. Of equal interest is the fact that solid is encountered in the bulk of the diagram. The phase diagram also shows the relationships between solid formation and gas content particularly in the part of the phase diagram near the maltene apex - the region of greatest interest in the present context. For a gas content less than 10 wt %, solid or other phase formation is not encountered up to high asphaltene concentrations (~ 40 wt %), while at higher gas concentrations multiphase behavior arises in the 0.3 to 5 wt % asphaltene range.

**The Impact of Maltene Composition on the Phase Behavior of Reservoir Fluids.** In order to place the phase behavior of a reservoir fluid in a more general context, one must examine the impact of maltene composition on the reservoir fluid phase diagram. The simplest way to access the key features of the maltene or Oil I – Oil II axis, is to examine phase diagrams for whole heavy oil and bitumen or their fractions + diluents. Guo et al. show many asphaltene precipitation examples with sharp phase behavior transitions.
along the trajectory noted in Figure 5. The phase behavior noted in Figure 2, which follows a similar trajectory, shows that there are equally sharp fluid phase transitions. These sharp transitions are not anticipated in computational phase behavior models for reservoir fluids and this helps explain the inability of these models to predict as opposed to correlate the phase behavior of reservoir fluids. A second contributing factor, addressed elsewhere, is that equation of state models for the phase behavior of aromatic-alkane binary mixtures and by extension for more complex mixtures frequently do not predict the phase behavior of such systems adequately, i.e., the wrong phase behavior class is predicted.

Figure 5. Composition trajectories exemplified by the phase behavior noted on Figure 2 and by the asphaltene titrations performed by Guo et al.

Conclusions
Selection of a minimum of four pseudo components, chosen to reflect the key features of the phase behavior for both reservoir fluids and heavy oils, facilitates a unified approach for the construction of phase diagrams for both types of fluids and provides a sound basis for the development of predictive mathematical models for their phase behavior. Using this approach, one is able to construct semi-quantitative phase boundaries for complex systems where data are sparse and to place phase behavior observations in context. Further, such diagrams facilitate extrapolation of observed phase behavior to other conditions (pressures, temperatures, compositions) where data are unavailable and by extension the phase behavior of related fluids is also elucidated. In the absence of a coordinated approach for phase diagram construction phase behavior prediction for reservoir fluids and heavy oils will continue to enjoy limited success.

Acknowledgement
Financial support from the sponsors of the research chair (AERI, Albion Sands Energy Inc., CMG, CONOCO, DBR group of companies, Esso, Nexen, NRC, NSERC, Petroleum Society, Schlumberger,Syncrude Canada Ltd.) is gratefully acknowledged.

References