

Phase Behavior of Propane/Crude Oil Mixture in Supercritical Fluid Extraction

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Studies of petroleum asphaltenes have gained considerable attention in the past decades due to the increase of heavy crude oils. The reduction of light crude oil reservoirs and the increasing light oil demand, forced the petroleum industry to develop upgrading processes for raw materials and residues. The crudes contain large amounts of asphaltenes and resins. Supercritical fluid extraction (SFE) has found application in solvent extraction, separation processes and in the upgrading of petroleum feedstocks. The SFE concept is also of interest in enhanced oil recovery processes since the performance of these processes depends on the extraction of oil typically in a supercritical state. The Residuum Oil Supercritical Extraction (ROSETM) use of paraffinic solvents to upgrade heavy oils to produce deasphalting oil suitable. The deasphalted oil and the solvent are heated further to a supercritical state and the deasphalted oil is separated from the solvent. For design and evaluation of supercritical fluid extraction process, it is necessary to have reliable phase behavior data. The lack of information available in the literature concerning asphaltene's properties through a thermodynamic approach, for separation processes, makes it necessary to intensify the scientific contributions in that aspect. This work presents a phase behavior study for the separation of Oil-Asphaltene mixtures using supercritical propane. The selection of propane as a solvent for this system is due to its excellent solvent power and good selectivity. The phase behavior of the ternary mixture was modeled by using the Predictive Soave-Redlich-Kwong (PSRK). The ternary diagrams generated to illustrate the system's behavior were constructed throughout variations in pressure and temperature around the solvent's critical point. Furthermore, pseudo-components are also evaluated and compared with the ternary mixture, where a molecule of asphaltene must be created through group contribution method. These results were very important to establish the simulation ambient to the virtual supercritical deasphalting plant.

Keywords: Deasphalting, Supercritical, Heavy Crude, Propane

1. Introduction

Crude oil is a complex mixture of hydrocarbons, with small amounts of sulphur, oxygen and nitrogen, as well as various metallic constituents, particularly vanadium, nickel, iron and copper (Speight, 1999). In a dispersion medium consisting mainly of hydrocarbons, which can be classified into alkanes, naphthenes and aromatics, there are two groups of dispersed colloidal particles in solution: asphaltenes and petroleum resins. Asphaltenes are hydrocarbons with higher molar masses, and contain the majority of oxygen and sulphur compounds, inorganic and organic salts as well as the main part of the metal compounds. Reduction of asphaltenes and metal content can be achieved by disturbing the solvation equilibrium via addition of suitable solvents, e.g., propane, pentane, heptane or carbon dioxide, resulting in the flocculation of asphaltenes (Eckermann and Vogelpohl, 1990).

The solvent deasphaltation treats the residue of the vacuum distillation through a pressurized liquid-liquid extraction, using specific properties of the solvent. The deasphaltation produces the deasphalted oil and the asphalted residue (Mendes *et al.*, 2005). The Residuum Oil Supercritical Extraction process is the premier deasphalting technology available in industry today. This state-of-art process extracts high-quality deasphalted oil (DAO) from atmospheric or vacuum residues and other feedstocks. The asphaltene products from the ROSE process is often blended to fuel oil, but can also be used in the production of asphaltic blending components, solid fuels, or fuel emulsions. The development of the deasphaltation technology using supercritical fluid appears as a solution to improve the separation of the deasphalted oil (ODES) from the asphaltenes. The use of supercritical fluid has some advantages like: the difference of the densities between the extraction phase and the refining phase is greater than that obtained by the conventional liquid extraction, becoming the separation between the phases easier; the mass transport is faster using the supercritical fluid; the quantity and the quality of the ODES can be easily controlled adjusting the temperature and the pressure of the extraction system and the efficiency to recover the oil is a function of the density of the supercritical fluid (Mendes *et al.*, 2005). The knowledge of a proper thermodynamic modeling for mixtures of hydrocarbons in high pressures is extremely important for diverse applications in the petroleum engineering, such as reservoir simulation at high pressures and evaluation of extraction techniques of oil in deep waters.

2. Thermodynamic Modelling of Supercritical Phase behavior

Regardless the modelling procedure, the following thermodynamic relationships, or their equivalent relationships, in terms of chemical potential must be satisfied so that two phases be in phase equilibrium.

$$f_i^v(T, P, y_i) = f_i^l(T, P, x_i) \quad (1)$$

where, f_i^L is the fugacity of component i in the liquid phase, f_i^V is the fugacity of component i in the vapour phase, x_i is the mole fraction of component i in the liquid phase and y_i is the mole fraction of component i in the vapour or SCF phase. The most computationally straightforward and thermodynamically consistent method for calculating high-pressure phase behaviour is to choose an equation of state to model

both the liquid and vapour or SCF phases. With this approach, the fugacity in each phase can be written as:

$$f_i^L(T, P, x_i) = x_i \phi_i^L P \quad (2)$$

$$f_i^V(T, P, y_i) = y_i \phi_i^V P \quad (3)$$

where, ϕ_i^L is the fugacity coefficient of component i in the liquid phase, P is the system pressure, T is the system temperature and ϕ_i^V is the fugacity coefficient of component i in the vapour phase. This is the ϕ - ϕ thermodynamic approach. The γ - ϕ models (γ being the activity coefficient) can not be used for phase equilibrium with supercritical fluids due to the manner that it treats each phase in different ways; therefore, it can not represent in continuous form the changes that occur in the critical region. This inconsistency is not present in the EOS models (Equation of State), where the fugacity equality for vapour-liquid equilibrium is written with ϕ - ϕ models.

The fugacity coefficients can be calculated from the exact thermodynamic relationships:

$$\ln \phi_i^V = \frac{1}{RT} \int_{V_i}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j \neq n_i} - \frac{RT}{V} \right] dV - \ln \left(\frac{P V_i^V}{RT} \right) \quad (4)$$

$$\ln \phi_i^L = \frac{1}{RT} \int_{V_i^L}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j \neq n_i} - \frac{RT}{V} \right] dV - \ln \left(\frac{P V_i^L}{RT} \right) \quad (5)$$

where R is the gas constant, v^V is the molar volume of the vapour phase, v^L is the molar volume of the liquid phase, and n_i and n_j are the number of moles of components i and j , respectively. To determine the analytical form of $\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j \neq n_i}$, a single equation

of state (EOS) can be used. Fortunately, in many cases, high-pressure phase behaviour can be reasonably represented with an EOS if the components in the mixture do not differ substantially in size, structure or in shape. The most commonly used cubic EOS are the Soave-Redlich-Kwong (SRK) equations and Peng-Robinson (PR) equations.

In this work, the model used is the Predictive Soave-Redlich-Kwong equation of state (PSRK), which is an extension of the SRK equation of state. This model uses the Holderbaum-Gmehling mixing rules; these rules can predict the binary interactions at any pressure. The PSRK method is predictive for any interaction that can be predicted by UNIFAC at low pressure. The main advantage of using PSRK equation of state is that it is more accurate in prediction of the binary interaction parameters and it gives more satisfactory results for mixtures of non-polar and polar components, as the case of the asphaltenes-oil mixture. The Holderbaum-Gmehling mixing rules use a relationship between the excess Helmholtz energy and equation-of-state. The goal of these mixing rules is to be able to use binary interaction parameters for activity coefficient models at any pressure. They do not use a relationship between equation-of-state properties and excess Gibbs energy, as in the Huron-Vidal mixing rules.

These mixing rules applied to an EOS, allow the prediction of the vapour-liquid equilibrium for a great variety of systems, without the addition of new parameters to the model. The Holderbaum-Gmehling mixing rules are used along with the PR EOS for

prediction of the volatility and density properties of gasoline.

2.1 Holderbaum-Gmehling mixing rules for PSRK model

The pressure-explicit expression for the equation-of-state is substituted in the thermodynamic equation:

$$P = - \left(\frac{\partial A}{\partial V} \right)_T \quad (6)$$

The Helmholtz energy is calculated by integration and A^E is obtained by:

$$A_m^E = A_m - \sum_i x_i A_i^* - RT \sum_i x_i \ln x_i \quad (7)$$

where both A_i^* and A_m are calculated by using equation 1. A_i^* and A_m are written in terms of equation-of-state parameters. The simplified form of constant packing fraction (V_m/b) is used:

$$\frac{V_i^{*l}}{b_i} = \frac{V_m^l}{b} \quad (8)$$

with:

$$b = \sum_i x_i b_i \quad (9)$$

Therefore:

$$V_m^E(p = \infty) = 0 \quad (10)$$

The mixing rule is:

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{1}{\Lambda^*} A_m^E(p) \quad (11)$$

where, Λ^* is slightly different from Λ for the Huron-Vidal mixing rule:

$$\Lambda^* = \frac{1}{\lambda_1 - \lambda_2} \ln \left(\frac{\frac{V_m}{b} + \lambda_1}{\frac{V_m}{b} + \lambda_2} \right) \quad (12)$$

where, λ_1 and λ_2 depend on the equation-of-state. In general, a cubic equation-of-state can be written as:

$$P = \frac{RT}{V_m - b} - \frac{a}{(V + \lambda_1 b) + (V_m + \lambda_2 b)} \quad (13)$$

If equation (11) is applied at infinite pressure, the packing fraction goes to 1, so that $\lambda_1 = 1$ and $\lambda_2 = 0$ for the SRK equation of state. The excess Helmholtz energy is equal to the excess Gibbs energy.

3. Results a Discussion

The graphs were constructed in three different conditions for the solvent: subcritical, near critical and supercritical, in order to verify the phase-behavior in these extraction conditions with propane (Figure 1).

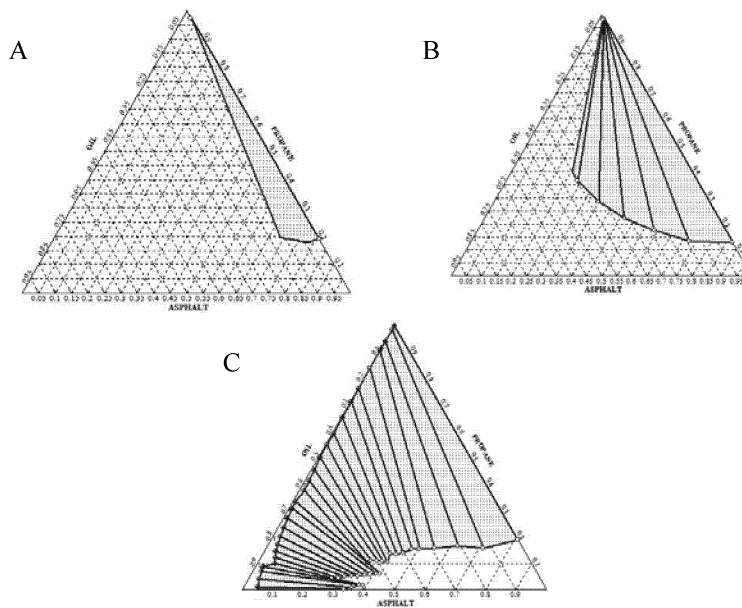


Figure 1 – Ternary diagrams asphaltenes-oil-propane (heavy Canadian asphaltene) : A – P = 1500 kPa, T = 303.15 K (subcritical), B- P = 2400 kPa, T = 338.15 K (near critical) e C – P = 6000 kPa, T = 368.15 K (supercritical).

Analyzing the ternary diagrams, it can be concluded that the behavior of this system is qualitatively similar to that described by (Wilson *et al.*, 1936) for the same system propane-oil-asphalt, as already described and illustrated in Figure 3. Figure 3A shows at 303.15 K and 1500 kPa, what means, in subcritical conditions, the oil is totally miscible with asphalt and the propane is partially miscible with asphalt, as it is shown by the region of immiscibility through the curve in the propane-asphalt axis, however propane presents large miscibility with the paraffinic phase (oil), therefore the asphaltenes are dropped out of the solution. This represents the first stage of the refining process of lube oil. Figure 3B shows that in a pressure slightly below to the critical pressure of the solvent (4100 kPa), there is an expansion in the two-phase region of the diagram, thus the liquid propane is in a more expanded state than at 1500 kPa.

If the system pressure, together with the temperature, is increased to a value above the critical point of the solvent, as shown in Figure 3C, the binary mixture oil-propane develops a vapour-liquid region on the oil-propane axis of the ternary diagram and a vapour-liquid-liquid region appears inside the diagram. The three-phase region appears because the supercritical condition of the solvent, the degree of separation seems to have considerably increased for a pressure above 4200 kPa (critical pressure of propane). In this stage, as it has an immiscibility between oil and propane, it is possible to separate the resins and the lightest fractions of the residue from the propane-oil mixture, due to the reduction of the density and to the solvent power of propane in these conditions, allowing a separation of the extract stream free of asphaltenes in DAO and

propane, which after some refining operations can be recycled to the process; this condition corresponds to the last stage of the ROSE process.

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5. Referens

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