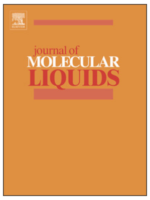
Journal of Molecular Liquids xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq



Estimation of asphaltene precipitation and equilibrium properties of hydrocarbon fluid phases using PC-SAFT equation of state

Morteza Sabeti [a], Aria Rahimbakhsh [b], Mohammad Nikookar [c,*], Amir H. Mohammadi [d,e,**]

[a] Department of Chemical Engineering, Isfahan University of Technology, Isfahan, Iran
[b] Department of Petroleum Engineering, Petroleum University of Technology, Ahwaz, Iran
[c] Department of Chemical Engineering, Tarbiat Modares University, Tehran, Iran
[d] Institut de Recherche en Génie Chimique et Pétrolier (IRGCP), Paris Cedex, France
[e] Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa

ARTICLE INFO

Article history:
Received 28 January 2015
Received in revised form 23 April 2015
Accepted 3 May 2015
Available online xxxx

Keywords:
PC-SAFT
Phase equilibrium
Asphaltene precipitation
EOS
Thermodynamic properties

ABSTRACT

Most of the components of heavy oil contain coarse grained molecules and it is impossible to estimate the density and phase behavior of such fluids by cubic equations of state (EOSs). Meanwhile, equations of Statistical Associated Fluid Theory (SAFT) have shown much success due to their high ability to calculate fluid's density. Among them is the PC-SAFT theory which despite being introduced about a decade ago, has not been vastly used in the industry and commercial software packages. In this survey, an alternative to describe fluids containing coarse grained molecules in high pressures is presented, using the PC-SAFT theory. Then, some properties of oil such as fluid's density, bubble- and dew point, phase envelop and asphaltene precipitation, are estimated by declaring the definition of applicable algorithms. Precipitation of asphaltene in different stages of crude oil production causes formation damage, choking in pipe lines and wells and the production system. Therefore, estimating the asphaltene behavior in a crude oil looks vital. One of the major purposes of the present work is to investigate the asphaltene phase behavior which is solely accomplished by modeling as a function of temperature, pressure and composition. Despite the previous SAFT modeling, the method of calculating the amount of asphaltene precipitation is based on the solid model. Qualitatively, this model is compared with experimental data which are obtained from adjoining a solvent (nC_5 to nC_9) with heavy oil, to observe its prosperity in predicting asphaltene precipitation. In this comparison, the average error percentage yielded an interval of 5 to 12% for the asphaltene precipitation weight percentage. Except the association term, the repulsive and attractive molecular interaction terms are considered for the present approach. Therefore, the model input includes the oil pseudo-components, PC-SAFT parameters and interaction coefficients between components. To model asphaltene precipitation using the PC-SAFT equation of state, the system is considered as vapor–liquid–quasi-liquid so that its equilibrium helps modeling, considering asphaltene as a quasi-liquid pure phase. The main privilege of estimating asphaltene precipitation by the method presented in this study over the solid model is that it does not need to adjust the volume shift parameter, whereas it is essential when using cubic EOSs.

1. Introduction

The modeling of phase equilibrium and thermodynamic properties of hydrocarbon phases or phase behaviors of fluids requires a reliable method so that researchers can optimize the best condition for production. Generally, there are two categories of models by which scientists successfully carry out the computations of fluid properties such as those of densities, phase equilibrium and prediction of hydrocarbon components asphaltene precipitation. The first one is a cubic equation of state (EOS). Commercial software packages usually use sorts of EOS models in their phase behavior estimations. Among the most favorable EOSs are the Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK) equations that fail to estimate adequate results for aromatics at high pressures in the presence of polymers with polar or associating solvents and generally a volume correction is needed to match results with those obtained by EOSs [1]. Prediction of the thermodynamic properties of such systems is appealing to industry. Therefore, the second group of models which is based on Statistical Associated Fluid Theory (SAFT) EOS, can be a suitable substitute for the cubic EOSs in which a volume correction is not needed to match the SAFT equation of state with experimental PVT data [1].

---

* Corresponding author.
** Correspondence to: A.H. Mohammadi, Institut de Recherche en Génie Chimique et Pétrolier (IRGCP), Paris Cedex, France.
E-mail addresses: mohamad_ni@yahoo.com (M. Nikookar), a.h.m@irgcp.fr, amir_h_mohammadi@yahoo.com (A.H. Mohammadi).

http://dx.doi.org/10.1016/j.molliq.2015.05.003
0167-7322/© 2015 Published by Elsevier B.V.

Please cite this article as: M. Sabeti, et al., Estimation of asphaltene precipitation and equilibrium properties of hydrocarbon fluid phases using PC-SAFT equation of state, J. Mol. Liq. (2015), http://dx.doi.org/10.1016/j.molliq.2015.05.003

SAFT is a molecular approach to demonstrate macroscopic systems and so far has had limited applications in chemical engineering. It can be declared that the first article about application of SAFT was published by Chapman and co-workers in the 1990s [2,3] that was based on the first order perturbation theory of Wertheim [4]. In SAFT theory, the Helmholtz free energy of components is totally introduced with the sum of hard sphere repulsion, dispersion interactions, chain connectivity and association terms. This theory defines fluid as molecules with chain of bonded spherical segments. The physical parameters required for calculating properties of fluid involve the number of segments in a chain molecule, volume of a segment and the segment–segment Van der Waals attraction. The SAFT equation also has the ability to predict the association interaction between each of the molecules, but it needs at least two more parameters for each associating component. The SAFT model can be applied to numerous groups of components such as amphiphilics, aromatics, polymers and alcohols to obtain their phase behaviors [5]. Many years later after introduction of SAFT, modified equations such as S-SAFT, soft-SAFT, MS-SAFT and PC-SAFT in the aim of promoting the calculation procedure of the SAFT terms were presented by authors [6–9]. At the first, the perturbed chain SAFT (PC-SAFT) equation of state was invented by Gross and Sadowski in 2001. PC-SAFT is the promotion of SAFT and is somehow derived based on it. Because a hard chain fluid serves as a reference for perturbation theory rather than the spherical molecules, in the PC-SAFT the dispersion energy depends on a mixture of hard chains not only on hard spheres. PC-SAFT has wide use in modeling phase equilibriums and phase behaviors of mixtures of alkanes, branched alkanes, cycloalkanes and other hydrocarbon compound series [9,10]. Recently, the studies about PC-SAFT have been developed, especially by introducing new methods to determine PC-SAFT parameters for the heavy end components of reservoir fluids [1,11,12]. But among its most important applications, PC-SAFT can reliably be applied to polymers and coarse-grained molecules such as asphaltenes.

Crude oil is a mixture of several hydrocarbons and other compounds and in a famous category, these components are listed into saturates, aromatics, resins and asphaltenes (SARA) [13–15]. Asphaltene is referred to heavy and highly viscous materials that can exist in petroleum reservoir fluids and cause choking in wells and pipelines [14,16,17]. Asphaltenes contain simple heteroatoms (C, H, N, O, and S) accompanied, most times, by metal constituents (Fe, Ni, and V) having aromatic cyclic structures with alkyl side chains [13–15]. Asphaltene is often insoluble in n-pentane and n-heptane in room temperature, but is highly soluble in benzene and toluene. More information about nature of other oil fractions (saturates, aromatics and resins) exists at previous literatures [13,14].

Changes of operational conditions such as pressure and temperature as well as fluid composition changes can develop the opportunity of asphaltene precipitation. Specifically, the effect of temperature on asphaltene stability is an issue under survey and study. The influence of temperature increase on solubility of asphaltene has been investigated by several authors and different results have been reported [18–21]. Deeper investigations revealed that the very specific effect of temperature is on the parameter of asphaltene solubility in oil. For example, Verdier et al. [22] injected CO_2 to two oil samples in different conditions and proved that the parameter of asphaltene and oil solubility is a function of temperature and by use of an appropriate approximation, they found the effect of temperature on solubility of asphaltene. By this explanation, they showed that such controversial views about the temperature influence on the amount of asphaltene precipitation can be justified by the Le Chatelier Principle and the solubility parameter. Asphaltene precipitation occurs in a bounded region called asphaltene deposition enveloped (ADE). This region is qualitatively shown in Fig. 1 for an oil sample in P vs. mole–solvent coordinates in a constant temperature. As the oil pressure drops during production above the bubble point of some crude oils, especially those containing high fractions of saturates, asphaltenes may precipitate. During enhanced oil recovery when compressed gases, such as methane (or natural gas) or carbon dioxide, are injected into the reservoir, asphaltenes may also precipitate because it alters the reservoir fluid characterization [13]. The boundary between oil–asphaltene and oil–gas–asphaltene which is on the fluid's bubble point, includes the maximum amount of asphaltene precipitation [23–25].

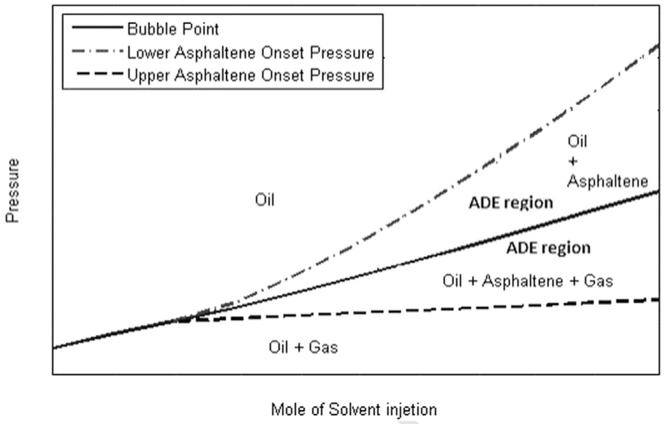


Fig. 1. Qualitative view of asphaltene deposition enveloped region in pressure vs. mole of solvent.

There are many definitions to describe the nature of asphaltene [26] of which some assume asphaltene as a solid phase [27,28] and some take it as a class of highly viscous liquids [29–31]. Authors attributed the asphaltene precipitated phase to operation temperature, where solid phase would appear into crude oil at room temperature, while the liquid state appears at higher temperatures [24,32]. This latter point of view even exists in reversibility of asphaltene precipitation. Some authors believe that the precipitated asphaltene is irreversible and thus cannot return to a soluble state, while others oppositely have admitted the possibility of secondary asphaltene precipitation solubility in rich oil [33,34]. Hirschberg et al. indicated [24] that the reversibility of asphaltene precipitation with changing the pressure at high temperatures. Most of the investigators claimed the reversibility of asphaltene precipitation at high temperatures while changing the pressure and composition [29,32,35,36]. But it is an irreversible, or, from a kinetic point of view, slow reversible process at low temperatures [16]. Generally, it is believed, the formation of asphaltene particles is a two-step process. At first, asphaltene particles separate from oil phase and then, flocculate and grow into aggregate substances, eventually resulting in asphaltene precipitation [37].

Due to such controversial views about mechanisms of asphaltene precipitation formation, it is not unpredictable to face a huge number of submitted papers about predicting the amount of asphaltene precipitation. The complex and not yet clearly understood physics of asphaltene causes the assumption that most theoretical investigations regard asphaltene as one single pseudo-component, instead of mixed substances [14,38]. Mohammadi and coworkers [13,39] generally divided the thermodynamic models for estimating formed asphaltene precipitation into five classes: "activity coefficient-based models", "EOS-based models", "colloidal/micellization-models", "scaling laws" and "association models". One of the most prevalent offered models (activity coefficient-based models) is the Flory–Huggins [40] model that takes advantage of equations of state (EOSs) to calculate the liquid phase mole fraction and solubility. This model was first developed for polymer solutions only, but was modified later by researchers such as Mohammadi, Nikookar and others [13,14,24,41–45] to determine the effects of pressure and composition on the onset conditions and the amounts of the precipitations, and was thus applied to materials other than polymer solutions. In this field, several researchers [46–48] conducted various experiments in different conditions on heavy oils of different fields around the world and replaced EOSs by correlations found

Please cite this article as: M. Sabeti, et al., Estimation of asphaltene precipitation and equilibrium properties of hydrocarbon fluid phases using PC-SAFT equation of state, J. Mol. Liq. (2015), http://dx.doi.org/10.1016/j.molliq.2015.05.003