Asphaltene precipitation in live crude oil during natural depletion: Experimental investigation and modeling

Shahin Kord[1], Shahab Ayatollahi*

Enhanced Oil Recovery (EOR) Research Center, School of Chemical and Petroleum Engineering, Shiraz University, P.O. Box 7134851154, Shiraz, Iran

ARTICLE INFO

ABSTRACT

The complicated nature of asphaltene molecules besides the unknown mechanism of phase separation of asphaltene-containing systems as well as lack of a suitable characterization parameter has questioned the generality of the available thermodynamic models.

The scaling equation developed by Rassamdana et al. [10,13] and its generalized form presented by Hu et al. [20] proved existence of a general relationship to model the asphaltene precipitation envelope and the onset. However, it works only for dead oil systems; here it has been tried to extend this technique for live oil fluids at reservoir condition. In this study, three types of experiments were conducted on five live reservoir fluid samples. The samples were collected from a giant Iranian oil field to measure the amount of precipitated asphaltene for a wide range of temperature and pressure.

The results of this study developed a new live oil scaling equation and successfully applied to predict a new real data-set. The predictions of the model were compared with the two widely used thermodynamic methods of single component solid and modified Flory–Huggins (FH) models. The results show that the phase stability and the regions where asphaltene precipitates from the live crude oil were predicted using this new scaling equation with an acceptable accuracy.

1. Introduction

Almost in all stages of oil production and transportation, the petroleum industry suffers from separation of a heavy organic matter called "asphaltene." Asphaltenes refer to the fraction of crude oil insoluble in excess normal alkanes such as n-pentane or n-heptane, but soluble in benzene or toluene at room temperature; compared to resins which are the fraction of crude oil insoluble in liquid propane but soluble in n-pentane at ambient conditions [1–3]. Considering a sample of oil, it always has been desired to know "when," "where," "how much," and "under what conditions" asphaltene precipitates as a solid phase out of the solution [4,5]. Crude oil is commonly divided into four chemically distinct fractions: saturates, aromatics, asphaltenes, and resins [6]. More or less, all crude oils contain the asphaltene fraction, so the question is "why do some of them with small fraction, face asphaltene separation during production while others do not?"

One of the fundamental difficulties encountered in describing the phase behavior of asphaltene-containing systems is lack of a suitable characterization parameter [7]. Besides, the state of the asphaltene particles in the petroleum is doubtful. Depending on the asphaltene polarity and presence of other compounds (paraffins, aromatics, resins, etc.) in the crude oil, asphaltene particles are believed to be dissolved partly in the crude and partly in steric-colloidal and/or micellar forms [8,9]. Being certain about each of these states depends on the reversibility of the process of asphaltene separation from the solution. In the case of "solution theory," molecular thermodynamics can be used, and in this category the most prevalent thermodynamic approach to describing asphaltene solubility has been the application of the solubility parameter or the concept of cohesion energy density [7]. The more the difference between the solubility parameter of the solvent and the asphaltene is, the more asphaltene precipitation forms. Therefore, this difference may be defined as the precipitation potential of a system. The precipitation potential of an aromatic solvent is close to zero and therefore, it can fully dissolve more asphaltene species [10]. A cycloparaffin with the same number of carbon atoms as a normal alkane can dissolve more asphaltene species, since the difference between the solubility parameter of the asphaltene and that of a cycloparaffin is less than that between the asphaltene and the normal alkane [10].

* Corresponding author. Present address: Sharif University of Technology, Iran. Tel.: +98 711 6474602; fax: +98 711 6473575.
 E-mail addresses: kord@shirazu.ac.ir (S. Kord), shahab@shirazu.ac.ir, dr.ayatollahi@gmail.com (S. Ayatollahi).
[1] Tel.: +98 711 6474602.

Table 1
Composition and condition of crude oil samples (#1–5).

Component	Crude oil samples				
	1	2	3	4	(Test crude #5)
H_2S	1.39	0.16	1.72	0.43	2.04
CO_2	5.18	1.55	3.68	2.45	4.36
N_2	0.88	0.45	0.19	0.22	0.22
C_1	22.57	22.9	24.27	25.82	22.21
C_2	6.94	7.64	7.42	7.92	6.84
C_3	5.91	5.35	5.39	5.62	5.11
$i\text{-}C_4$	0.98	1.16	0.93	1	0.84
$n\text{-}C_4$	2.97	2.74	2.71	2.85	2.48
$i\text{-}C_5$	0.93	0.93	0.9	1	0.81
$n\text{-}C_5$	1.03	1.12	1.04	1.17	0.95
C_6	3.07	4.27	3.21	1.31	0.92
C_7	4.06	4.29	4.62	6.6	6.36
C_8	4.14	3.6	3.62	4.59	4.36
C_9	3.69	3.31	3.3	4.26	2.62
C_{10}	3.45	2.95	2.18	3.32	3.16
C_{11}	2.11	2.72	2.52	2.92	2.33
$C_{12}{}^+$	30.7	34.86	32.3	28.52	34.39
Total	100	100	100	100	100
Sample depth (mss)	4139.1	3339.34	3754.24	3266.14	3706.85
Reservoir temperature (°C)	123.89	104.44	123.89	104.44	121.11
Bubble point pressure (MPa)	12.72	11.09	13.10	11.84	13.13
API gravity stock tank oil	24.46	20.75	19.85	22.71	20.93
Live oil molecular weight	138	165	158	160	143
C_{12+}					
MW	326	370	378	420	310
SG	0.9355	0.9599	0.9652	0.9437	0.9637

On the other hand, some theories support the irreversibility of asphaltene precipitation process [11] as it demonstrates that it is impossible to completely re-dissolve the asphaltene precipitated during titration. Besides, some independent tests [10,12] support the idea that the asphaltene precipitation process is at least "partially" reversible.

Besides the reversible and irreversible models, other approaches have been employed to study the asphaltene precipitation from petroleum fluids such as the scaling equations [12–17]. Rassamdana et al. [18] presented a scaling equation based on ideas of Park and Mansoori [19] who found asphaltene precipitation to some extent similar to aggregation/gelation phenomena.

This simple model was capable of successfully predicting asphaltene titration experiments at standard conditions. Hu et al. [20,21] checked the scaling equation against the precipitation data available in the literature. They also examined the universality of exponents Z and Z', the main coefficients used in the scaling equation. It was concluded that $Z' = -2$ is a universal constant regardless of oil composition and the type of the solvent, and the optimum value of Z varies between 0.1 and 0.5. In Iran, some major oil fields such as Ahwaz, Mansuri, Ab-Taymur, and Kupal have the asphaltene problem. Since treating the deposited asphaltene is too expensive and in some cases impossible (i.e., formation damage), in the current situation, mitigation and prevention of asphaltene precipitation and deposition is the main strategy proposed by the industry experts. Therefore, having an accurate model for predicting the amount of asphaltene precipitation during pressure, temperature, or composition changes seems essential. As large asphaltene molecules resemble the polymers in molecular structure and distribution as well as in polarity distribution, two well-known thermodynamic models of single component solid and modified Flory–Huggins (FH) are incorporated. The results show that the phase stability and also the regions where asphaltene precipitates from petroleum fluids cannot be predicted accurately by these models. The main objective of this work is to develop a scaling equation which, on one hand does not require the complicated and local calculations of the thermodynamic models, and on the other hand, leads to the expected results by a simple but highly precise

approach for a wide range of pressure and temperature. To achieve this, in the first step, as described in Section 2, three types of tests were performed on some Iranian crude oil samples for wide pressure and temperature ranges; similar works can rarely be found in the literature for live oils.

The validity of the model proposed here for predicting the amount of asphaltene precipitating from a crude oil was checked against the model developed by Hirschberg [22]. Besides, in Section 3.2, this model along with its modified form is compared with the single-component solid model. In Section 4.1, through our experimental study, a powerful scaling equation is obtained which can accurately predict asphaltene precipitation for wide ranges of pressure and temperature. Finally, in a comparative study, the results of the proposed model are checked against the well-known thermodynamic models.

2. Experimental work

In order to mimic the reservoir conditions and check the possibility of fluid grading in the reservoir, five different regions were selected and the reservoir fluid samples were taken by downhole fluid sampling technique. All the experiments were performed on the live oil taken under the reservoir temperature and pressure. Three types of experiments (complete PVT experiments, SARA analysis, and asphaltene precipitation) were performed on the five different crude oil samples to find their composition, molecular weight, SARA fraction, PVT data, and the potential of asphaltene precipitation at different pressures (Table 1).

2.1. SARA analysis and asphaltene content determination

SARA test is conventionally used for crude oil characterization. On this basis, the oil is characterized for saturates (S), aromatics (A), resins (R), and asphaltene (A), as described by the Institute of Petroleum [23]. The amount of asphaltene which precipitates from a crude oil under atmospheric conditions is usually considered as the crude asphaltene content. This value strongly depends on the type of the solvent used for precipitation. To have a reference