Inhibiting asphaltene precipitation from Iranian crude oil using various dispersants: Experimental investigation through viscometry and thermodynamic modelling

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ABSTRACT

Asphaltene precipitation is a major assurance problem posing significant technical and economic loss on petroleum industry. To tackle this issue, various treatments have been proposed and applied by industry. Amongst, inhibiting or retarding the asphaltene precipitation has been understood as the most efficient approach. In this regard, blending crude oil with chemical additives could appreciably heighten its stability. Surfactants, owing to amphiphilic nature, could keep asphaltene dissolved in crude oil by precluding self-tendency of those particles to making agglomerates. Despite importance of this subject, there is still lack of sufficient experimental data to evaluate effectiveness of different inhibitors for oils of various regions, in particular Iran. Therefore, our research group made effort to investigate performance of different oil soluble additives for enhancing stability of asphaltene in Iranian crude oil through measuring onset of asphaltene precipitation using viscometry method.

This study presents complementary data to our previous works as well as providing a deep discussion to compare influence of toluene, linear and branched dodecyl benzene sulfonic acid (DBSA) and coca-mide diethanolamine (CDEA). It was realized that inhibition characteristic is driven by the synergy between strength of polar head and tail length of chemicals, as well as inhibitor concentration in the oil phase. In this respect, this work suggests the following priority order for selecting inhibitors: Linear-DBSA > CDEA > Branched-DBSA > Toluene.

In the second part of this work, the measured onset points were predicted through coupling Peng-Robison (PR) with Dehaghani association equation of state (DA-EOS). The applied model gave successful prediction via taking asphaltene self-association and asphaltene-inhibitor cross association into account.

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1. Introduction

Asphaltene precipitation is a major disaster occurring almost in all parts of oil industry, from reservoir to refinery unit [1]. It has been well recognized that asphaltene deposition is prone to plug rock's pore throats, resulting in formation damage and subsequently losing well deliverability [2]. Also, deposition in drill string or well head facilities could lead to technical and economic issues and even, in worst case, unexpected shutdown [3]. In past decades, researchers and industrial specialists have made attempts to devise efficient preventive treatments for asphaltene precipitation [4].

Amongst, using inhibitors has been proved to be the best remedy for avoiding or postponing asphaltene drop out [5].

Generally, asphaltene cannot be defined precisely [6]. In fact, asphaltene is classified as the heaviest fraction of crude oil possessing polynuclear (condensed) aromatic rings with alkyl (aliphatic) side chains and polar functional groups [7]. From a practical point of view, the term asphaltene is defined as that portion of a crude oil being precipitated once diluting with normal alkanes (mostly n-pentane or n-heptane); while aromatic solvents such as toluene and xylene improve its stability [8]. In accord with this operational definition, traditionally, asphaltene content is reported as amount of hydrocarbon precipitation after mixing a given oil sample with normal alkane, usually n-heptane [9].

To date, there is no consensus over microscopic distinction of

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asphaltene molecules, yet [6]. No universal criterion has ever offered to distinguish asphaltene molecules individually [10]. However, as macroscopic behavior of a given crude oil is in directly associated with state of its constituting species, so one needs at least a conceptual model to relate asphaltene stability to its inter-action with other species in hydrocarbon media [11]. In this way, colloidal theory has found great attention [12]. According to this theory, asphaltene is described as heavy organic components which are likely to agglomerate through their lyophobic (polar) sites [12,13]. In this sense, asphaltene are naturally distributed as small agglomerates, analogous to what happens in aqueous colloidal solutions [14]. Further, to maintain their stability, resin plays the role of a stabilizer adsorbing on periphery of asphaltenes and impeding their further self-association [15]. Upon this theory, any process disturbing (or weakening) resin task might lead to asphaltene precipitation. By contrast, adding resin-liked com-pounds to crude oil, could improve asphaltene stability, which is the focus of this paper.

Till now, various methods have been proposed to measure onset of asphaltene precipitation (in short OAP) [10]. Escobedo and Mansoori devised a viscometry technique being able to identify OAP for both types of light and heavy (black) crude oils [16]. In their approach, an oil sample is gradually blended with a precipitant, e.g., n-heptane, while simultaneously measuring its viscosity. According to their philosophy, asphaltene flocculation is associated with producing big agglomerates (flocs) which renders oil a sharp in-crease in viscosity. In this sense, one could simply ascertain OAP as the first point of deviation (sharp break) in the trend of oil viscosity versus solvent concentration added to the crude. This method is advantageously simple and could be easily utilized for different kinds of crude oil [17]. Shadman et al. applied viscometry to investigate inhibition of asphaltene-induced precipitation by different amphiphiles, including branched- and linear-dodecyl benzene sulfonic acid (DBSA) [18]. They pointed out asphaltene stability is directly proportional to amphiphile concentration mixed with crude oil. Most importantly, it was realized that specification and characteristics of the given oil, for example amount of different fractions in particular resin, and also chemical structure of amphiphile, control effectiveness of chemical additives. In past years, many studies were devoted to establishing an inter-relationship between oil and amphiphile properties with inhibi-tion efficiency based on measurement of onset point [13,19—21]. Leon et al. studied adsorption of alkylbenzene-derived amphphiles on asphaltene particles [22]. They suggested a two-stage process for this phenomenon. In their observations, first, additive particles adsorb individually on asphaltene surface. Then, at the second step, amphiphiles self-interaction leads to further accumulation of peptizing agents at the asphaltene covered area. They came to the conclusion that inhibition strength largely depends on maximum amount of stabilizer adsorbed on asphaltene aggregates.

In another study, to improve stability of Brazilian crude oil, Gonzalez and Middea assayed peptizing ability of alkyl-benzene derived materials with focus on functionality of hydroxyl and amide polar groups [23]. In this case, nonyl phenol was observed to be the best dispersing agent. They attributed asphaltene dispersion to direct interaction between polar head of amphiphiles and polar sites located on asphaltene molecule. Besides this direct conclusion, they inferred asphaltene stabilization to be the result of amphiphile association with their molecules. In this scheme, aromatic moieties of asphaltene could act as electron donors to neutralize polar head of chemical additives [23].

In a comprehensive study, Al-Sahhaf et al. investigated inhibi-tion efficiency of deasphalted oil (DO), extracted resin, toluene and three types of surfactant while adding to Kuwaiti crude oil [19]. In their study, DO and toluene proved to be inefficient needing

extraordinary concentration to give appreciable inhibition effect. By contrast, owing to their polar head acidity, surfactants retarded OAP at lower concentration. It was recognized that, for Kuwaiti crude oil, peptizing strength is directly associated with acidity (nature and number of functional groups) of the amphiphile used. In a similar investigation on Kuwaiti oil, Ghloum et al. utilized three types of inhibitors (both commercial and non-commercial) and came to similar conclusions [24].

Through measuring zeta potential and electrophoretic mobility of two kinds of Chinese residue oil, Wang et al. observed vital role of the asphaltene electric property [25]. To obtain optimum inhibition performance in terms of amphiphile-asphaltene interaction, they asserted negatively charged asphaltenes should be peptized with cationic inhibitors and vice versa. This would partly neutralize asphaltene polarity, which makes it more compatible with non-polar media of hydrocarbon phase [25].

Junior et al. made use of commercial surfactants as well as vegetable oils and their derivatives to increase onset of asphaltene flocculation in Brazilin oil while being diluted with aliphatic sol-vents (n-heptane and n-pentane) [21]. They pointed out stabilizing capacity of an amphiphile is controlled by balance between polarity (lyophobic) and hydrocarbon chain length. In other words, having sole strong polar heads does not essentially correlate with amphi-phile strength to disperse asphaltene particles. For example, as observed by Junior et al. salicylic acid even resulted in asphaltene destabilization [21].

Until now, different experimental studies have been conducted in an attempt to establish a generic correlation for inter-relashionship between characteristics of asphaltene and inhibitor, and also composition of a given oil sample. In spite of discussed works, there is a huge gap to thoroughly identify effect of chemical inhibitors on asphaltene stabilization, yet. After an extensive liter-ature survey, authors realized a conspicuous paucity of released information on the asphaltene stabilization of Iranian crude oils using chemical inhibitors. In this regard, our research group is investigating interaction between different oil soluble inhibitors and Iranian crude oil.

This work presents complementary data to out earlier works [18,26—28] along with deep discussion on effectiveness of various chemicals (toluene, linear and branched- DBSA, and CDEA) for peptizing asphaltenes in Iranian crude oil. In remainder of this paper, first, we explain the experimental technique of our work and then, the measured onset points will be compared based on char-acteristics of additives.

2. Experiment

2.1. Materials

Two dead oil samples, hereafter called Oil I and Oil II were used to analysis their asphaltene stability. Tables 1 and 2 present iden-tifications and composition of the oil samples, respectively. Also, Fig. 1 shows viscosity and density of the crude oils at varying temperatures. To verify our measurements, asphaltene content was obtained through SARA test and IP 143 standard method; both

Table 1
SARA (saturate, aromatic, resin, and asphaltene) fraction of oil samples used in experiments.

Crude Oil	Density (API)	SARA test				IP143
		Saturates	Aromatics	Resins	Asphaltene	Asphaltene
Oil I	17.96	30.79	42.10	13.36	13.75	13.75
Oil II	17.62	46.63	34.30	4.77	14.30	14.30