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Temperature effects on solubility of asphaltenes in crude oils

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A B S T R A C T

Asphaltenes, the heaviest fraction in crude oil, are linked to severe problems in petroleum industry. Asphaltenes are either in dissolved state or in colloidal dispersion form in crude oil. Temperature has a significant role in dissolving the asphaltenes in continuous phase of crude oil. However, there are differing views on the effect of temperature on solubility and precipitation of asphaltenes. In this work, an investigation was carried out on the effect of temperature on solubility of asphaltenes for six different crude oil samples in the temperature range of 20–95 °C, using automated flocculation onset titration. The test results are interpreted in terms of the Heithaus parameters and using Hildebrand's solubility parameter. The experimental data, the Heithaus parameters and the Hildebrand solubility parameter show that solubility of asphaltenes increased with increase in temperature and possible phase transition of asphaltenes takes place with the increase in temperature.

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Keywords: Asphaltenes; Precipitation; Solubility; Heithaus parameters; Hildebrand solubility parameter; Automated flocculation titrimeter

1. Introduction

Asphaltenes are the heaviest and most complex molecules in crude oil and are defined by its solubility class as the constituents of oil which are soluble in toluene but insoluble in n-heptane. Presence of asphaltenes in crude oil has been linked to several problems in petroleum industry. Much of the research has been driven by the tendency of asphaltenes to aggregate, precipitate and deposit onto surfaces (Arciniegas and Babadagli, 2014; Hoepfner et al., 2013; Mullins et al., 2007; Spiecker et al., 2003; Maqbool et al., 2011). Deposit formation in crude oil processing can be attributed to various factors but asphaltenes are generally considered as main precursors of deposit formation on heat transfer surfaces in crude oil processing (Hoepfner et al., 2013; Murphy and Campbell, 1992; Wiehe, 2006). The presence of asphaltenes on heat transfer surfaces further favors fouling of equipment because asphaltenes are more prone to attach to already coked

surfaces than a clean metallic alloy surface (Asprino et al., 2005). In order to mitigate problems caused by asphaltenes, a thorough understanding of the process of asphaltenes precipitation, flocculation and deposition and the factors affecting them is necessary (Macchietto et al., 2011; Mohammadi and Richon, 2008; Srinivasan, 2008; Wiehe, 2008). Factors, such as, temperature, pressure and crude oil composition have been observed to effect asphaltenes solubility and precipitation (Crittenden et al., 2009; Deshannavar et al., 2010; Ramasamy and Deshannavar, 2014; Watkinson, 2003).

Whether a change in temperature dissolves asphaltenes in oil or it favors precipitation of asphaltenes from oil; and whether the asphaltenes exist in crude oil in dispersed state forming a colloidal suspension of oil or they exist in dissolved state in oil like a true solution, are still debatable. There are different schools of thoughts on relationship between phase behavior of asphaltenes and change in temperature. Some studies (Branco et al., 2001; Chung, 1992) show that a part of asphaltenes in oil is dissolved and the rest of asphaltenes is in colloidal dispersed form (Bartholdy and

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Nomenclature

C	concentration (g/mL)
FR	flocculation ratio
P	Heithaus compatibility parameter
P_o	peptizing power of oil
P_a	peptizability of asphaltenes
T_p	time to flocculation peak (s)
T	temperature (°C)
V	molar volume (mL/mol)
V_o	volume of oil (mL)
V_s	volume of solvent (mL)
V_T	volume of titrant (mL)
v_T	volumetric flow rate of titrant (mL/s)
W	weight (g)
δ_{as}	solubility parameter of asphaltenes (MPa ^{0.5})
δ_F	solubility parameter of solvent–titrant mixture (MPa ^{0.5})
δ_m	solubility parameter of mixture (MPa ^{0.5})
δ_o	solubility parameter of oil (MPa ^{0.5})
δ_s	solubility parameter of solvent (MPa ^{0.5})
δ_T	solubility parameter of titrant (MPa ^{0.5})
ϕ_o	volume fraction of oil
ϕ_s	volume fraction of solvent
ϕ_T	volume fraction of titrant

Andersen, 2000; Gharfeh et al., 2004). Chung (1992) stated that asphaltenes can either precipitate or dissolve in crude oil on changing thermodynamic conditions such as temperature. According to Mansoori (1997), asphaltenes appears in crude oil both as soluble phase and as well as colloidal one and asphaltenes deposition from petroleum fluids is partly due to solubility effect and partly due to colloidal phenomenon. The asphaltenes colloids are considered as molecules in a true solution and are also reported to be thermodynamically a liquid phase at higher temperature, forming liquid–liquid equilibrium with oil phase (Akbarzadeh et al., 2005; Chung, 1992; Ganeeva et al., 2014; Mansoori, 1997; Pan and Firoozabadi, 2000).

Mathematical modeling has been used in predicting asphaltenes precipitation and solubility. Some of the models are based on colloidal dispersed state of asphaltenes and some are based on the existence of asphaltenes in liquid state in crude oil. Firstly, Hirschberg et al. (1984), by using Flory–Huggins polymer solutions theory and definition of asphaltene solubility as a reversible phenomenon, presented a new model for asphaltenes precipitation. Leontaritis and Mansoori (1987) proposed a model predicting the onset of asphaltene flocculation in which asphaltenes exist in the oil as solid particles in colloidal suspension, stabilized by resins adsorbed on their surface. Rassamdana et al. (1996) proposed scaling equation based on partial aggregation and dissolution phenomenon of asphaltenes. Akbarzadeh et al. (2005) used a generalized regular solution model for their data to estimate asphaltenes precipitation from *n*-alkane diluted heavy oils and bitumen.

Mehranfar et al. (2014) used atomic force microscopy to observe the structural changes in asphaltene nano-aggregates as a function of temperature (25–80 °C), demonstrating the transition of asphaltenes to liquid phase with increase in temperature above 70 °C. Maqbool et al. (2011) used optical microscopy to evaluate the effect of temperature on

asphaltenes precipitation kinetics. They presented a hypothesis that destabilized asphaltenes aggregate more at 50 °C than at 20 °C but precipitation rate is lower due to lesser number of particle collisions because of the higher aggregate size.

Hu and Guo (2001) studied the effect of temperature and molecular weight of *n*-alkanes on asphaltenes precipitation using flocculation onset titration method along with light scattering technique, and their data show that amount of asphaltenes precipitation was higher at 20 °C than at 65 °C. Laux et al. (1997) used flocculation onset titration coupled with light transmission technique to investigate the influences of different factors on stability of colloid disperses in crude oils. They studied the effect of temperature on flocculation onset point using polar and non-polar titrants in the temperature range of 0–50 °C and concluded that there was no significant effect of temperature on flocculation onset point.

Andersen and Stenby (1996) precipitated and then re-dissolved asphaltenes in *n*-heptane-toluene solution to study thermodynamics of asphaltenes precipitation in the temperature range of 24–80 °C and observed that asphaltenes solubility increased with the increase in temperature and increase in concentration of toluene in *n*-heptane-toluene solution. According to a study by Lambourn and Durrieu (1983), dependence of asphaltenes solubility on temperature was observed, where asphaltenes dissolved between 100 and 140 °C temperature range but re-precipitated above 200 °C. Storm et al. (1996) established similar conclusions in their rheological and small-angle x-ray scattering study on asphaltenes flocculation that asphaltenes flocculate at 150–200 °C and the flocculation is purely a physical phenomenon not a chemical one. But Wiehe's (1997) hot-stage microscopy results are somewhat differing from the above two, according to which insoluble asphaltenes re-dissolve in residue on heating from room temperature to 200 °C. This was in agreement with Hong and Watkinson's (2004) study on solubility and precipitation of asphaltenes carried out in the bulk temperature range of 60–300 °C. In the study it was observed that the concentration of dissolved asphaltenes increased at higher temperature and it was suggested that, for deposition and fouling studies, the concentration of suspended asphaltenes is important than the dissolved ones. Evdokimov et al. (2003) diluted virgin crude oil in toluene to observe asphaltenes aggregation in their viscosities, optical and NMR studies. Based on their results of the studies, the authors concluded that the molecular aggregation in crude oil solutions is a sequential process, which leads to a phase transformation to liquid.

A suitable approach to investigate influences of different factors on the stability of colloidal dispersion is to determine flocculation onset point in crude oil (Andersen and Stenby, 1996; Cimino et al., 1995; Mofidi and Edalat, 2006). Solubility of asphaltenes depends on the solvating power of the solvent (Chung, 1992). This is in agreement with Hildebrand and Scott's (1962) theory of regular solution which is a widely used theory to interpret asphaltenes precipitation. According to the theory, the solubility of one component in a mixture affects the solubility of other components. This is further substantiated by Wiehe's (1996) investigation on asphaltenes solubility which shows that asphaltenes are more soluble in the solvent having higher field force solubility parameter.

Several types of laboratory units and techniques have been reported to be used in the study of asphaltenes solubility and precipitation. Some studies involved manual methods and others employed automated ones. The following

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