Investigation of Effect of Bulk Temperature on Dissolution and Precipitation of Asphaltenes Using Flocculation Onset Titration

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ABSTRACT

All of the organic fouling in petroleum refinery crude preheat train is caused by insoluble asphaltenes and the effect of bulk temperature on solubility of asphaltenes is somewhat uncertain. In this work, the effect of bulk temperature on flocculation and precipitation of asphaltenes in crude oil residue has been investigated at different temperatures from 20 ^{0}C to 95 ^{0}C using automated flocculation titrimeter. It is observed that the solubility parameter and solvating power of the oil increased with the increase in temperature. The results indicate that solubility of the particles in oil and overall stability of the oil increased with the increase in temperature in the range studied.

Keywords: Bulk Temperature, Asphaltenes, Flocculation, Precipitation, Titration

INTRODUCTION

The build-up of unwanted deposits on the heat transfer surfaces of heat exchangers is generally termed as fouling (Bott, 1995). Fouling has been a matter of great concern in crude oil production, processing and transportation. Significant developments have been made in understanding the mechanisms of crude oil fouling (Bott, 1995, Crittenden et al., 1992). Wiehe (2006) determined that 90% of the crude oil fouling is brought about by only a few common causes. Crude oil fouling is generally classified into organic and inorganic fouling. Inorganic fouling is a result of presence of impurities such as salts, corrosion products, minerals and clay (Bott, 1995). Asphaltenes play an important role in crude oil fouling and the entire organic fouling is due to insoluble asphaltenes (Wiehe, 2006, Murphy and Campbell, 1992). Yet, the effect of bulk temperature on asphaltenes solubility is not well established (Irwin A, 2008, Hong and Watkinson, 2004, Rastegari et al., 2004, Ramasamy and Deshannavar, 2012). There are differing views in the literature on the effect of bulk temperature on solubility of asphaltenes. Ramasamy and Deshannavar (2012) analysed the effect of bulk temperature on crude oil fouling concluded that asphaltenes dissolve at high bulk temperature with the help of fouling data reported in literature and their own experimental data. Lambourn and Durrieu (1983) observed that asphaltenes dissolve between 100 – 140 ^{0}C temperature range but re-precipitate above 200 ^{0}C. In their rheological and small-angle x-ray scattering study on asphaltenes flocculation, Storm et al. (1996) established comparable conclusions that asphaltenes flocculate at 150 - 200 ^{0}C. But hot-stage microscopy results of

Wiehi (1997) are somewhat differing from the above two, according to which insoluble asphaltenes re-dissolve in residue on heating from ambient temperature to 200 ^{0}C.

EXPERIMENTAL

Flocculation onset titration is a widely used technique to investigate the oil properties in terms of solubility parameters. Automated flocculation titrimeter by Koehler Instrument, model no. K57100 was employed to conduct the flocculation onset titration. Automated flocculation titration uses light transmission technique to measure the onset of flocculation by subjecting a solution to light transmittance, carried out through photo spectrometer, which is primarily employed as a turbidity detector. Light transmission has been employed by many researchers, e.g., Yang et al. (1999) used light transmission to investigate the effect of pressure on precipitation onset. Khoshandam & Alamdari (2010) used light transmission technique in measurement of asphaltenes concentration.

Asphalts and other heavy oil residua have been demonstrated as colloidal suspensions in which a polar, associated asphaltenes (the dispersed phase) was thought to be suspended in the dispersing or continuous medium of oil, the maltenes. The extent to which these two would remain in a given state of peptization was thought to be a measure of the compatibility or stability of the suspension according to J. J. Heithaus (1962). The solubility parameter at which asphaltenes just begin to precipitate and the solubility parameter of the whole oil can be calculated from flocculation onset titration data. To predict the colloidal stability of a system, three parameters of Heithaus titration method are calculated, which are P_a, P_o and P. P_a is a measure of peptizability of asphaltenes, the dispersion of asphaltenes to produce a colloidal dispersion or the tendency of asphaltenes to exist as a stable dispersion in an oil (ASTM, 2002). P_o is the solvating power of oil, the dispersing phase. P is the measure of colloidal stability of individual heavy oil or a blend of oils, which is determined by the former two parameters, P_a and P_o. The value of P lies between 2.5 and 10. The oils having lower value of P are considered to be incompatible and those having higher P value are designated to be compatible (ASTM, 2002). P_a and P_o are calculated from two other parameters, flocculation ratio (*FR*) and dilution concentration (*C*). The values of *FR* and *C* are obtained from the other experimental variables, weight of oil (*W*), volume of solvent (V_s) and volume of titrant (V_t) (Heithaus, 1960). Flocculation ratio (*FR*) is the minimum amount of solvent necessary to keep the asphaltenes dissolved in the solution (Heithaus, 1962). Dilution concentration (*C*) is the ratio of mass of residue to the volume of titrant and the volume of the solvent. A typical graph of flocculation ratio (*FR*) vs. dilution concentration (*C*) is shown in Fig. 1.

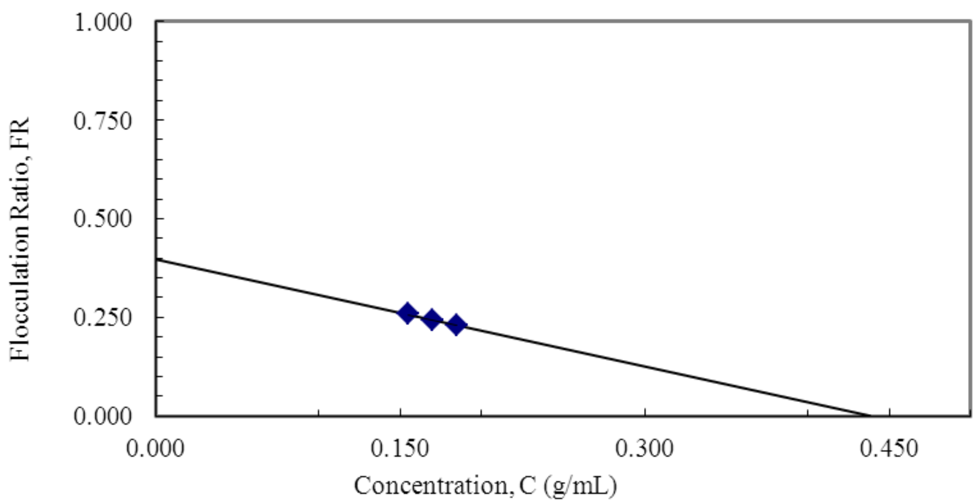

Figure 1. Flocculation Ratio vs. Dilution Concentration

The Y-axis intercept is $FR_{max.}$ The X-axis intercept is C_{min}, the minimum amount of titrant required to precipitate the asphaltenes from the oil solution.

Sample Preparation

Flocculation onset investigation was carried out for a crude oil having API gravity 27.97, termed hereafter as crude oil A. The crude oil was concentrated to 300+ ^{0}C using true-boiling point distillation method ASTM D2892 (ASTM, 2011). The flocculation onset titration tests were conducted at 20, 40, 60, 80 and 95 ^{0}C. For each test, three samples of the concentrated crude oil were prepared in 30-ml vials, each accurately weighed 1.2000 g, 1.4000 g and 1.6000 g, respectively. 2.000 ml of HPLC grade toluene was added in each sample to dissolve the oil in it. Each of these solutions was titrated with HPLC grade *iso*-octane (2, 2, 4-trimethyl pentane) obtained from Merck, contained in one of the two water jacketed reaction vessels.

Titration Procedure

Titration was carried out by inserting the 30-ml solution vial in a water jacketed vessel with continuous stirring using a magnetic stirrer. Temperature was controlled and maintained through circulation of water at ±0.5 ^{0}C tolerance of the set temperature. Titrant was dosed into the solution vial at constant flow rate of 0.410 ml/min, through a low flow rate metering pump. The solution was circulated continuously through 0.1 mm short path-length flow cell, housed in the photo spectrometer, to measure the percent light transmittance of the solution versus time at 740 nm radiation intensity of the light. Minimum volume of the titrant (V_t) to initiate flocculation is obtained based on the time (T_f) required to reach the onset point, the maximum % light transmittance (*%T*) after which the asphaltenes just begin to precipitate. Initially, the transmittance kept on increasing due to addition of titrant making the solution more dilute but decreased immediately after the flocculation onset peak was reached because of the increase in precipitation of asphaltenes which caused the increase in turbidity of the solution resulting in the decrease in the light transmittance.

Optical Microscopy

Optical microscopy is widely used in asphaltenes precipitation studies. Wiehe (2006) and Tabish et al. (2011) used optical microscopy for investigation of asphaltenes precipitation. Optical microscopy at 200X was used in this study to examine the solution after precipitation.

RESULTS & DISCUSSION

The data from automated flocculation titration tests show that light transmittance was higher in relatively more concentrated solution as shown in Fig. 2. The light transmittance decreased fairly in the solution having 1.6 g of oil than the solution having 1.2 g of the crude oil. It was because of the comparatively higher concentration of asphaltenes in 1.6 g sample. The samples were examined under a microscope at 200 times zoom and the precipitation was observed as is shown in Figs. 3

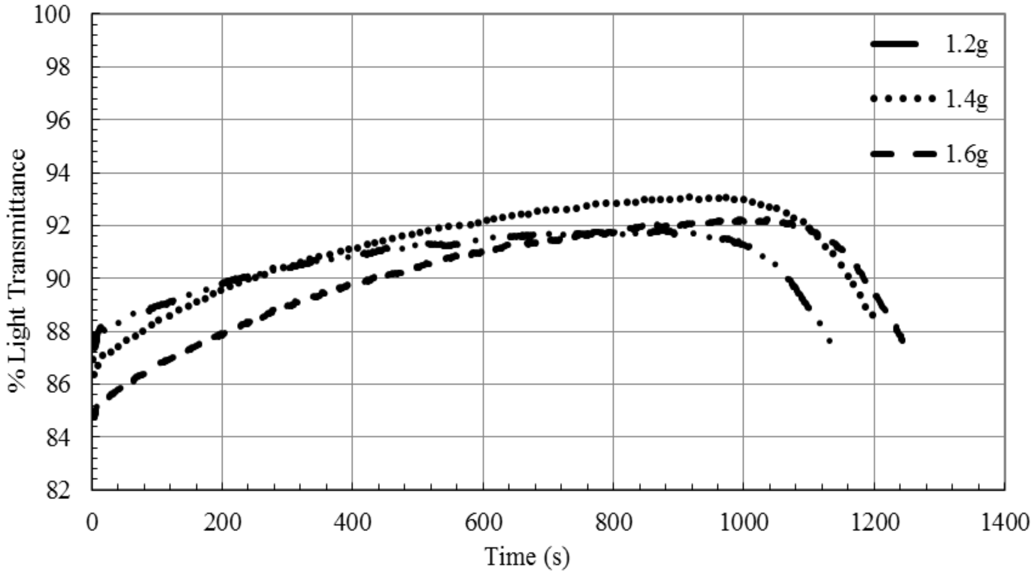

Figure 2. Light Transmittance in Oil A at 60 ^{0}C

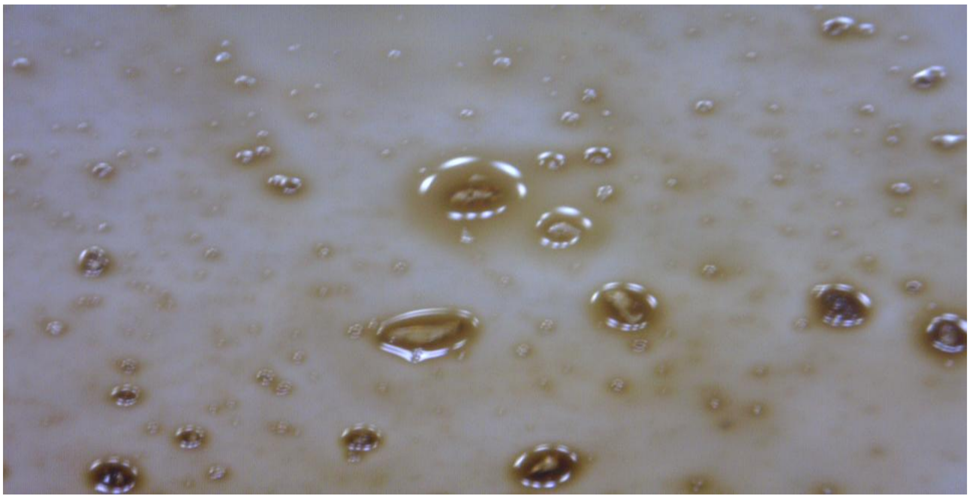

Figure 3. The micrograph of oil-solution precipitated after titration – 200X

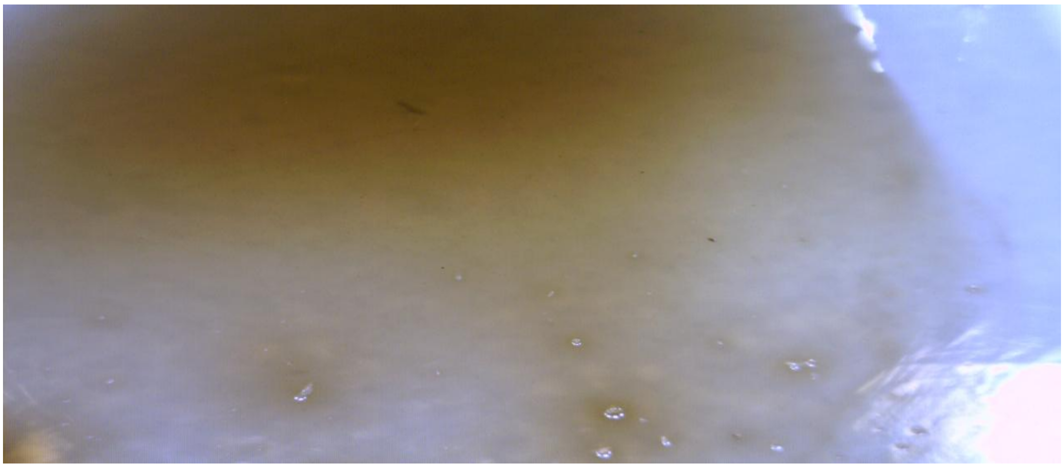

Figure 4. Toluene added in the precipitated solution

Further, toluene was added to verify the asphaltenes precipitation has taken place. The precipitated material dissolved immediately after addition of few drops of toluene in it as shown in Fig. 4 and then re-precipitated with addition of *n*-heptane confirming the presence of asphaltenes.

Disruption of the colloidal dispersion or peptizability of asphaltenes takes long time at a temperature of 20 ^{0}C. This is evident from the decreasing volume of the titrant and the time taken up to flocculation point with the increase in temperature as shown in Fig. 5. It took higher volume to break the interfacial tension between the asphaltenes colloids and the dispersing medium in the oil at lower temperature and vice versa. There is a possible phase transformation with the increase in temperature instigating more asphaltenes to dissolve in the solution hence the number of dispersed asphaltenes colloids becomes less and thus less volume of titrant is required to disrupt the interfacial forces between the colloids at higher temperature to cause the flocculation onset. This is further substantiated by the decrease in asphaltenes peptization, P_a, the stabilization of colloidal dispersion with the increase in temperature and the increase in solvating power of the oil, P_o and Heithaus parameter, P, with the increase in temperature as shown in Fig. 6.

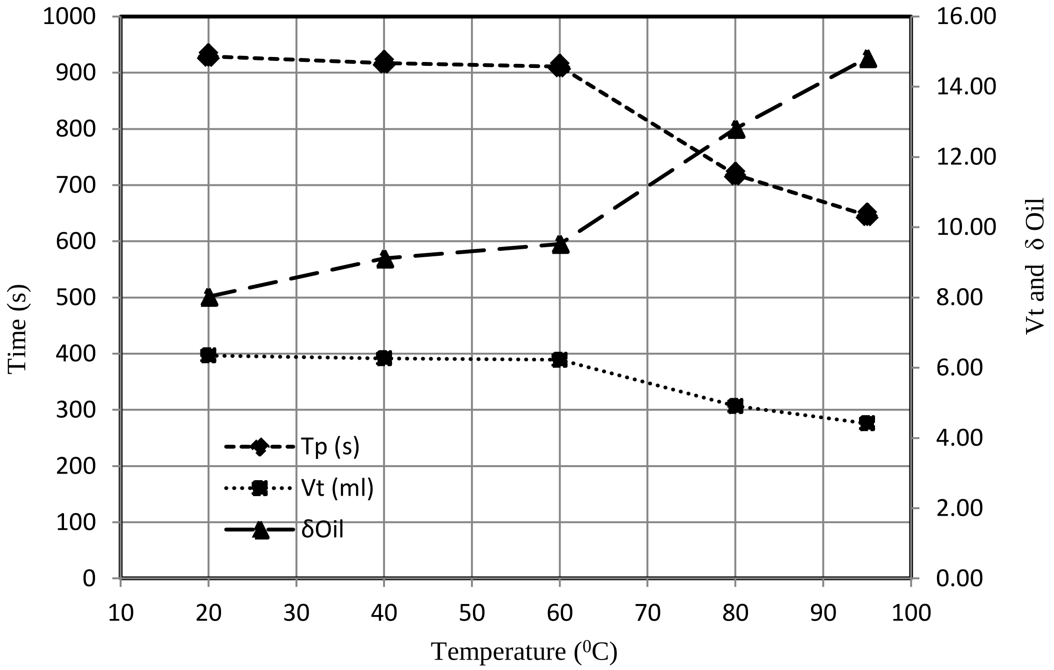

Figure 5. Flocculation Peak Time T_p, Titrant Volume V_t, and Solubility parameter δ, vs Temperature

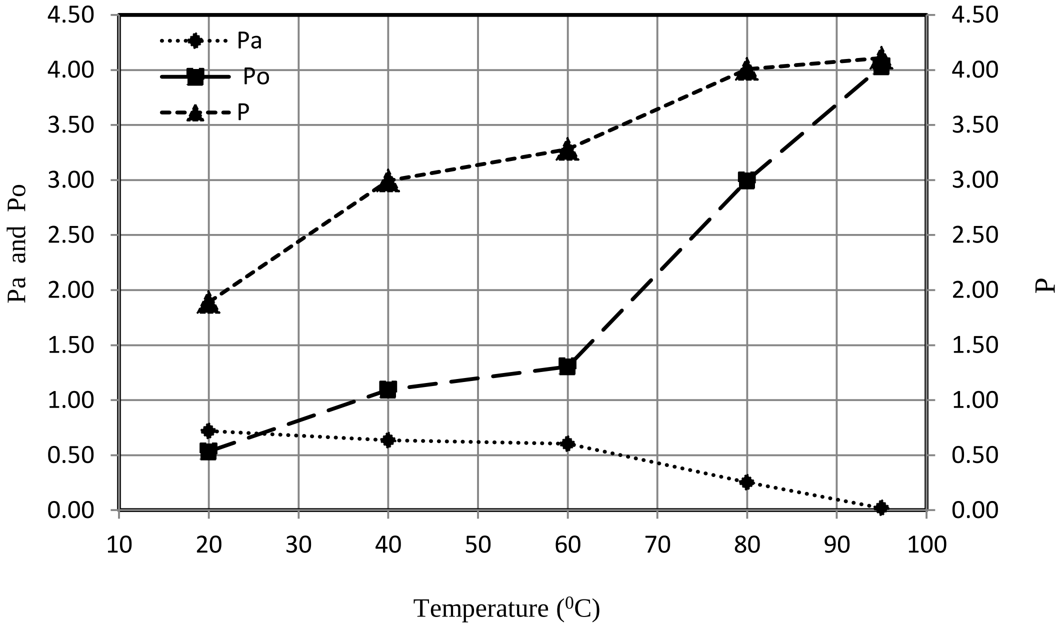

Figure 6. Peptizability of Asphaltenes P_a, Solvating Power of Oil P_o and Heithaus Parameter P vs Temperature

CONCLUSION

From the experimental results of asphaltenes peptizability, crude oil solvating power and the Heithaus parameter obtained from onset flocculation titration of three tests samples of the crude oil A, it is concluded that solubility of asphaltenes increased with the increase in bulk temperature of the oil solution, asphaltenes tend to flocculate slower at higher bulk temperature and over all solvating power of the oil also increased with the increase in bulk temperature of oil solution from 20 ^{0}C to 95 ^{0}C for the crude oil A. This leads to increased compatibility and stability of the crude oil with increase in the temperature range studied.

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