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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 study, the effect of bulk temperature on flocculation and precipitation of asphaltenes in crude oil residue has been investigated at different temperatures from 20-95°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.

Key words: 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, min-erals 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 (Wiehe, 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 *et al*. (1983) observed that asphaltenes dissolve between 100-140°C temperature range but re-precipitate above 200°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°C. But hot-stage microscopy results of Wiehe (1997) are somewhat differing from the above two, according to which insoluble asphaltenes redissolve in residue on heating from ambient temperature to 200°C.

MATERIALS AND METHODS

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 floc culation 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 and Alamdari (2010) used light transmission technique in measurement of asphaltenes concentration.

Asphaltenes and other heavy oil residue have been demonstrated as colloidal suspensions in which a polar, associated asphaltenes (the dispersed phase) was

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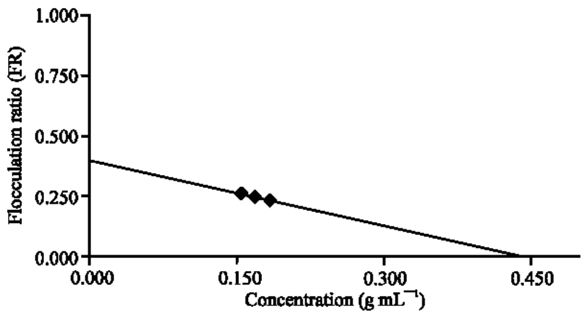

Fig. 1: Flocculation ratio vs. dilution concentration

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 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_0 and P.

The 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). The P_0 is the solvating power of oil, the dispersing phase. The 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_0. 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). The P_a and P_0 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 nec-essary 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.

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°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°C. For each test, three samples of the concentrated crude oil were prepared in 30 mL vials, each accurately weighed 1.2000, 1.4000 and 1.6000 g, respectively. The 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°C tolerance of the set temperature. Titrant was dosed in to the solution vial at constant flow rate of 0.410 mL min^{-1}, 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 Maqbool *et al.* (2011) used optical microscopy for investigation of asphaltenes precipita-tion. Optical microscopy at 200X was used in this study to examine the solution after precipitation.

RESULTS AND 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 1.6 g sample. The samples were examined

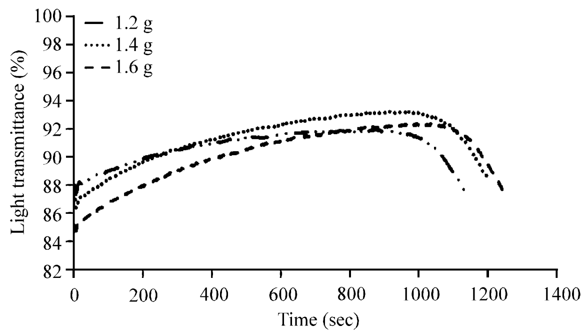

Fig. 2: Light transmittance in oil A at 60°C

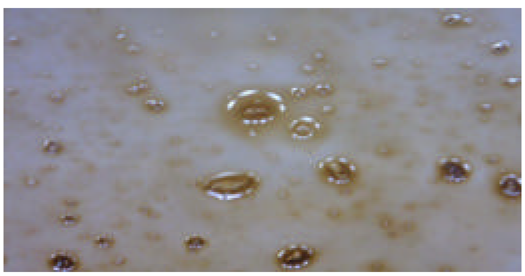

Fig. 3: Micrograph of oil-solution precipitated after titration, 200X

Fig. 4: Toluene added in the precipitated solution

under a microscope at 200 times zoom and the precipitation was observed as is shown in Fig. 3.

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°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

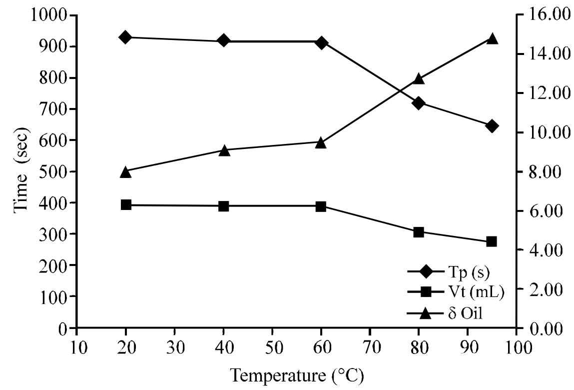

Fig. 5: Flocculation peak time T_p, titrant volume V_t and solubility parameter δ, vs. temperautre

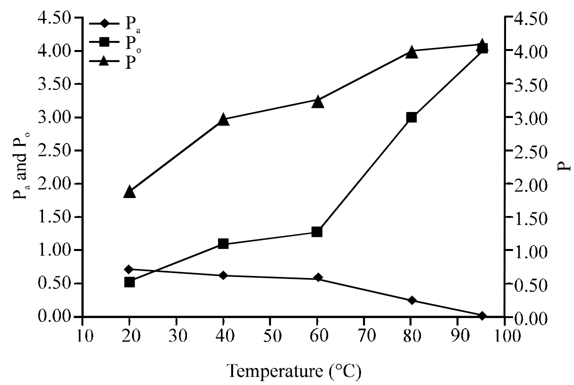

Fig. 6: Peptizability of asphaltenes P_a, solvating power of oil P_o and Heithaus parameter P vs. temperature

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.

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 20-95°C for the crude oil A. This leads to increased compati-bility and stability of the crude oil with increase in the temperature range studied.

ACKNOWLEDGMENT

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