The Effect of Compositional Changes of Binary Mixtures of n-alkane solvents on the Precipitation of Heavy Organics from a Solution of Crude Oil Residue

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ABSTRACT: The effect of precipitant compositional changes on the precipitation of heavy organics (HO) from a solution of crude oil residue using binary mixtures of n-alkane solvents was studied. Heavy organic precipitates were generated using different ratios of C_5:C_6, C_6:C_7 and C_5:C_7 n-alkane solvents. The result obtained showed that for binary mixtures at 1:0, 3:1, 2:1, 1:1, 1:2, 1:3 and 0:1 ratios, the weight percentage precipitates of C_5:C_6 were 11.19 ± 0.45, 8.56 ± 0.80, 5.62 ± 0.58, 8.53 ± 0.80, 5.83 ± 1.29, 5.45 ± 0.57 and 5.24 ± 0.32; C_5:C_7 were 11.19 ± 0.90, 5.63 ± 0.52, 2.12 ± 0.25, 4.51 ± 0.65, 2.11 ± 0.37, 1.67 ± 0.40 and 0.97 ± 0.05; and C_6:C_7 were 5.24 ± 0.32, 3.37 ± 0.08, 1.94 ± 0.03, 3.39 ± 0.60, 1.48 ± 0.03, 1.43 ± 0.03 and 0.97 ± 0.05 respectively. The results have shown that the quantity of HO precipitate decreases with increasing quantity of higher carbon number of n-alkane solvent to a minimum value at 2:1 ratio. From the minimum value, it rises to a maximum at 1:1 ratio as the proportion of C_{n+x} to C_n (where C is carbon atom, n and x represent the number of carbon atom) increases. The quantity of HO precipitate decreases again to a minimum at 1:2 ratio as the proportion of C_{n+x} increases further, and finally to the lowest value at pure C_{n+x}. The conclusion is that the components of the crude oil residue undergo a three-stage phase transition as the volume ratios of the n-alkane solvents vary. This study can lead to a better understanding of the phase behavior of heavy organics under compositional changes and hence the prediction of heavy organic precipitation. © JASEM

Introduction
Deposition, flocculation and plugging of heavy organics on petroleum pipelines, tubular, pumps and other equipment during production and transportation of petroleum fluids is a major problem in the oil industry. In most cases it has caused blockage in the oil reservoirs, pipelines and other tubular production and processing facilities hence leading to reservoir damage and reduction of well productivity. The problem has tremendous economic implications.

Arterial blockage in the petroleum industry is mostly due to the deposition of heavy organics from petroleum fluids (Pacheco-Sanchez and Mansoori, 1997). According to Escobedo and Mansoori (1992)**,** heavy organic deposition problem is one of the major factors that increases the production cost of petroleum products.

Over the years several studies have been conducted in attempt to proffer a lasting solution to the problem. More often, researchers approach the problem by trying to understand the causes of the deposition, mechanisms, nature and behavior of heavy organics under various operating conditions. Series of models

have been developed explaining the phenomena of heavy organic deposition (Mansoori, 1997; Branco et al., 2001; Hu et al. 2004; Mullins, et al. 2012).
In recent years, efforts have been directed towards precipitation of heavy organics in crude oil in the laboratory using single n-alkanes with the belief that results obtained would give a better understanding of the deposition phenomena, predict correctly the onset of organic deposition region and hence help to avoid getting to the region (Eduardo et al. 2004; Chapman et al. 2007; Saraji et al. 2013).

The study of asphaltene precipitation upon addition of *n*-alkane solvents to stock-tank oils has often been used in the understanding of the precipitation phenomena. Hirschberg et al. (1984) and Chung et al. (1991) reported a series of titration experiments in tank-oil samples with liquid alkanes from *n*-pentane to *n*-hexadecane as diluents, to determine the precipitation onset composition, the amount of material precipitated, and the solubility properties of asphaltenes. Kokal et al. (1992) reported the amount of asphaltenes precipitated when two Canadian heavy oils with a high content of asphaltenes were titrated with various *n*-alkanes (*n*-pentane to *n*-decane) at

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different dilution ratios. They observed that above a ratio of 10mls solvent/g oil, the precipitation is completed and also a decrease in the amount precipitated at very high dilution ratios was observed, which can be attributed, in part, to a partial re-dissolution of asphaltenes in the solvent.

Rassamdana and Sahimi (1996), measured the amount of precipitated asphaltene from an Iranian crude oil using normal alkanes with carbon number ranging from 5 to 10 at 25°C and atmospheric pressure. Eduardo et al. (2004), measured the precipitation of heavy organics in two Mexican crude oils and reported to have obtained a good prediction of asphaltene precipitation over a wide temperature, pressure and composition intervals by matching a single titration curve or two precipitation onset points with equation of state. Chukwu et al. (2011), precipitated heavy organics from Nigerian Antan crude oil residue using two slightly polar (C_x) solvents, ethyl acetate and butanone and compared their results with the quantity of precipitate by n-alkane non-polar solvents. They went further to conduct SARA (Saturates, Aromatics, Resins and Asphaltene) analysis to determine the composition of their precipitates.

In all these investigations, a common feature is that the amount of precipitated material decreases as the *n*-alkane carbon number of the solvent increases, and that complete precipitation is obtained above a certain solvent/oil ratio (typically between 10 and 30cm^3/g). Information from both the SARA analysis and the use of individual n-alkane solvents is not easily applicable to prediction of the tendency of a crude oil or a mixture of petroleum streams to precipitate heavy organic solids because crude oil is a complex mixture of hydrocarbon and all the n-alkane solvents are present in varied quantities for different crude oils.

This study therefore makes use of the binary mixtures of n-alkane solvents (n-hexane and n-heptane; n-pentane and n-heptane; n-pentane and n-hexane) at different ratios to precipitate heavy organics from crude oil to verify if the result obtained with the binary mixture precipitaton would be different from the use of individual n-alkane as a first step to extend the large amount of knowledge accumulated by the various researchers cited herein. A decision was taken to stop at washing the precipitate with the corresponding fresh mixture of n-alkanes to remove only adsorbed oil rather than the elaborate procedure by the ASTM (American Standard Test Method) and IP (Institute of petroleum) methods which focused on isolating specifically asphaltenes free from co-precipitated resins or wax. The precipitate is more likely to resemble the field heavy organics since no effort is made in this procedure to purify the precipitates. This study is more likely to yield results and conclusions that will lead to additional information which will be useful in solutions to real life field precipitation problems.

MATERIALS AND METHODS

Materials: The following materials were used: Nigerian Antan crude oil residue of 550°C AET (Atmospheric equivalent temperature), Tetrachloroethylene, n-pentane, n-hexane, n-heptane, Analytical balance model, AB54 Metter with accuracy of 0.0001g, Mechanical shaker (staurt flask shaker), Vacuum pump (leybold - heraeus pump), Membrane filter (0.45μm pore size, 47mm diameter), conical flasks, Buchner flasks, Buchner funnels, beakers, measuring cylinder, Thermo-stated oven, stop clock, stop corks, heating mantle, magnetic stirrer and stirring rods.

Methods: Nigerian Antan crude oil residue 550°C AET was collected from the Research and Development Division of Nigerian National Petroleum Corporation (NNPC), Port Harcourt, Nigeria. The solid residue was dissolved in tetrachloroethylene at 29°C and the tetrachloroethylene was evaporated by heating up to its boiling point at 121°C. Aliquots were collected from the bulk residue when necessary.

Precipitation using Binary Mixtures of n-hexane & n-heptane (C_6:C_7): The precipitation of heavy organics was carried out by precipitation experiments similar to those implemented by Kokal et al. (1992) and Eduardo et al. (2004) and modified ASTM/IP methods. 30mls of n-hexane and n-heptane binary mixtures at different ratios were added to approximately 1g of oil each in an appropriate flask. The mixtures were shaken for 30mins using mechanical shaker. It was allowed to stand for 48hrs. After which the solution was filtered using a vacuum pump system with a 0.45μm membrane filter fitted in a Buchner funnel/Buchner flask and connected to the vacuum pump. The flask and the membrane filter were rinsed with small volumes of the corresponding binary mixtures of n-alkane solvents (C_6:C_7) to eliminate the residual oil. The membrane filter with the precipitated material was dried in an oven over 2hrs. It was finally weighed to determine the heavy organic mass precipitate.

Precipitation using Binary Mixtures of n-pentane and n-hexane (C_5:C_6), n-pentane and n-heptane (C_5:C_7)
Heavy organics were also precipitated from crude oil using binary mixtures of C_5:C_6 and C_5:C_7. The same

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procedure used with C_6:C_7 binary mixture was also used here with high level of reproducibility. The quantities of precipitate weight percents in all cases were taken. The weight percents of the heavy organics at each corresponding ratio were determined using the relationship:

$$\text{Weight \%} = \frac{\text{Weight of HO precipitate in mg/L}}{\text{Weight of Residue in mg/L}} \times \frac{100}{1}$$

In all cases, the graphs relating the weight percents of HO to the solvent ratios (v/v) were plotted.

RESULTS AND DISCUSSION

The results of the experiments for the different ratios of C_6:C_7, C_5:C_7 and C_5:C_6 binary mixtures precipitated with approximately 1g of crude oil residue at room temperature and atmospheric equivalent pressure are given in Tables 1 to 3.

The C_6:C_7 binary mixture heavy organic precipitation experiment at different solvent ratios of 30mls/g total solvent volume (Table 1) recorded its highest percentage yield of precipitate (5.24±0.32) at 1:0 ratio (i.e.100% pure C_6) and least percentage precipitate (0.97±0.05) at 0:1 ratio (i.e.100% pure C_7). This trend which is also observed for C_5:C_6 and C_5:C_7 binary mixtures, is similar to the case of single solvents reported by various researchers (Mansoori, 1997; Branco et al., 2001; Hu et al. 2004; Eduardo et al, 2004; Chapman et al. 2007; Mullins, et al. 2012; Saraji et al. 2013. It is also in line with the previous reports that the quantity of heavy organics precipitated by n-alkane solvent decreases with increasing number of carbon atoms in the solvent. If the paraffinic compounds are good solvents for resins but not for asphaltenes, then as the volume of precipitant increases both the interaction between resins and asphaltenes and the capacity of the former to stabilize the asphaltene molecules as small aggregates becomes weak, causing asphaltenes to precipitate (Dubey and Waxman, 1995). Furthermore, since the interactions such as obstruction to movement or retardation between the n-alkane solvents molecules and the large heavy organic units will be small due to the difference in size and molecular weight, shielding effect of the polar units of the aromatics and resins is reduced (Branco et al., 2001). Tables 1, 2 and 3 show that the quantities of precipitate reduced sharply with decreasing ratios of lower carbon number to higher carbon number of n-alkane binary mixture from its highest at 3:1 to a minimum at 2:1 ratio. The precipitates then increased substantially and reached a maximum value at 1:1 ratio. Further addition of the higher carbon number of n-alkane solvents decreased the quantities of precipitates to the second minimum value at 1:2 ratios

and finally to the 100% pure higher carbon number of n-alkane solvent where the least percentage precipitate is recorded. This is attributed in part to the partial re-dissolution of asphaltene in the solvent mixture (Kokal et al.; 1992).

According to Escobedo and Mansoori (1992), asphaltene deposition is as a result of multi-phenomena effect which includes solid-liquid phase transition, colloidal formations and growth of colloidal formations and eventual collapse of the resulting colloids due to limitations on the size of the Brownian particles suspended in the media. This represents phase transition. The results obtained from the binary mixture experiment have demonstrated three stages of phase transition represented by points a, b and c as shown in the plots in figure 1.

Phase Transition of HOs in Crude Oil with n-alkane binary mixtures: *Solid-Liquid Phase Transition*: At pure C_n, some of the heavy organics are insoluble in the n-alkane diluted oil using a single solvent hence they appear in the solid phase. As C_{n+x} n-alkane solvent is added, part of the precipitated solid heavy organics redissolved in the liquid phase leading to a reduction in the value of the precipitate (Fig 1). At the first minima at 2:1 v/v ratio C_n/C_{n+x} dissolution of some precipitated components stop apparently. The reduction in the precipitate as C_{n+x} is added may be explained by the solubility of some resins or other heavy organics insoluble in pure C_n but soluble in C_{n+x}. In addition, some species which are co- precipitated with asphaltene may re-dissolve. The solid compositions along this line of equilibrium will differ significantly from the composition of the solid precipitated by pure n-alkane solvent.

Liquid-Solid Phase Transition: Precipitate formation begins to increase as the ratio C_n/C_{n+x} decreases further, i.e., as more C_{n+x} is added. This continues to the maximum at 1:1 ratio. As the volume of C_n:C_{n+x} approaches 1:1 ratio, colloidal formation and growth of colloidal particles probably occur leading to agglomeration and precipitation. This brings about the increase in the quantity of precipitate up to a maximum (maxima) at 1:1 ratio. The phase diagram (fig. 2) shows the transition of the soluble in liquid phase to the solid phase through colloidal formation.

Solid-Liquid Phase Transition: The third stage (fig. 2) shows the collapse of resulting colloids due to limitations on the size of the Brownian particles suspended in the media. The collapse begins as the volume of C_{n+x} exceeds C_n volumes and continues to 1:2 ratio of C_n:C_{n+x} where the second minimum is

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observed. Beyond this, there is very little change in quantity of the solid and liquid in equilibrium.

Conclusion: The following conclusions could be drawn from this study: (i) The quantity of HO precipitate decreases from the highest value for n-alkane of lower carbon number to a minimum value as the ratio of the n-alkane of higher carbon number increases. (ii) From the minimum value, it rises to a maximum as the proportion of C_{n+x} to C_n increases further. (iii) From the maximum value the quantity of HO precipitate (weight percent) decreases again to a minimum as the proportion of C_{n+x} increases further in the mixture of the two solvents. (iv) The two minima points for the quantities of HO precipitate are close to the quantity of HO precipitate obtained with solvent with the higher number of carbon atoms (C_{n+x},

where n, x are integers). (v) The maxima at 1:1 (v/v) ratio of the solvents are greater than the quantity of HO precipitate obtainable with the solvent of higher carbon atom but smaller than the quantity of HO obtainable with the lower carbon number; nearly approximating the average of the two. The minima were observed at solvent ratios of 1:2 and 2:1 (v/v) $C_n:C_{n+x}$ binary mixtures. On the whole, binary systems of solvents lead to phase changes of the heavy organics as the volume ratios of the n-alkane solvents vary. The multi-phenomena phase transition effects involved in heavy organic deposition which includes solid-liquid phase transition, colloidal formation and growth and eventual collapse of the colloids have been demonstrated through precipitation of heavy organics using binary mixtures of n-alkane solvents.

Table 1: Heavy Organics Precipitated by varied (v/v) ratios of n-C_6 and n-C_7 Binary Mixtures at 30ml/g of crude oil
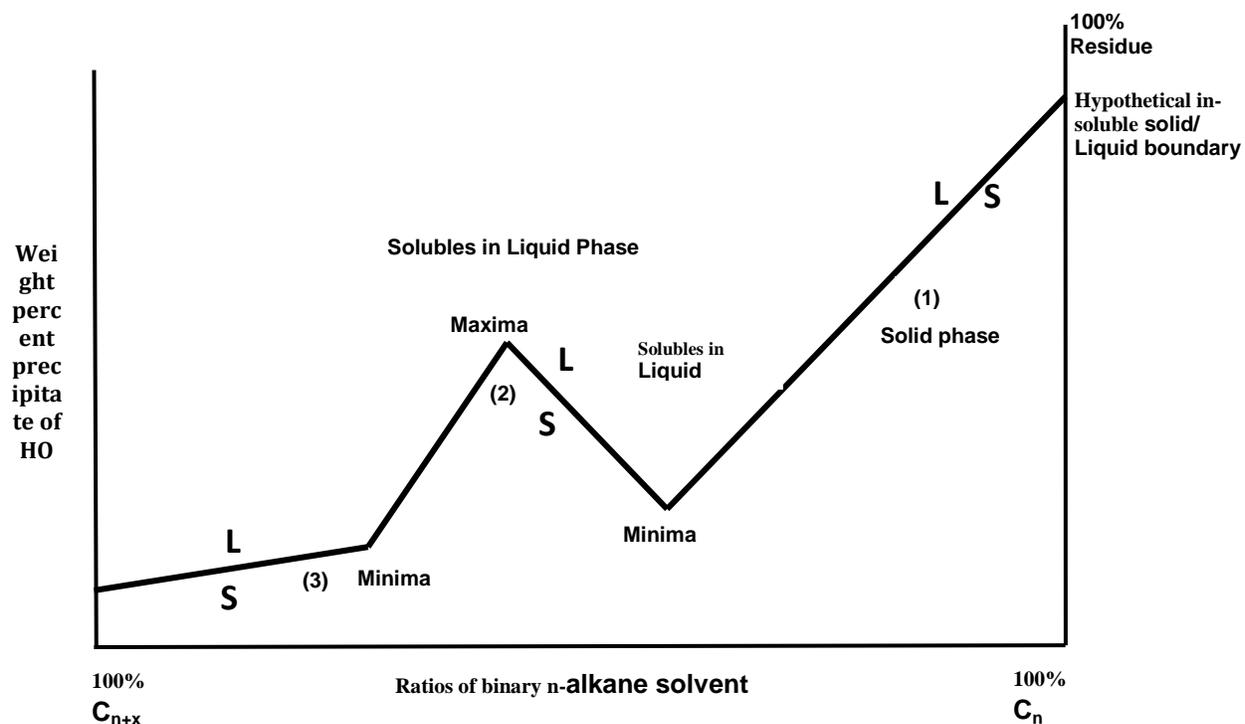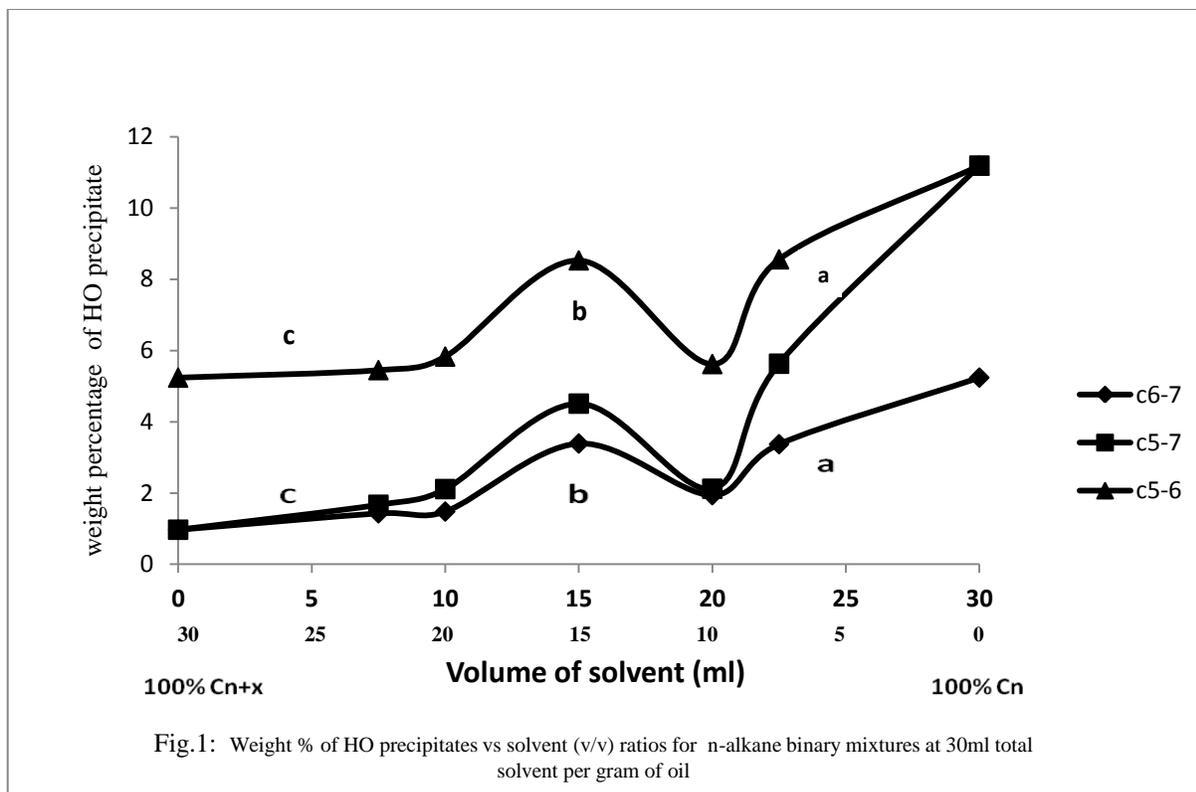
Test S/N	Solvent ratio $C_6:C_7$	v/v ratio (ml) $C_6:C_7$	Wt. of crude oil residue (g)	Wt. of HO precipitate (g)	Wt. % of HO ppt.
1	0 : 1	0 : 30	1.0423	0.0101	0.97 ± 0.05
2	1 : 3	7.5 : 22.5	1.0435	0.0149	1.43 ± 0.03
3	1 : 2	10 : 20	1.0243	0.0152	1.48 ± 0.03
4	1 : 1	15 : 15	1.0555	0.0358	3.39 ± 0.60
5	2 : 1	20 : 10	1.0600	0.0206	1.94 ± 0.03
6	3 : 1	22.5: 7.5	1.0902	0.0367	3.37 ± 0.08
7	1 : 0	30 : 0	1.0301	0.0540	5.24 ± 0.32

Table 2: Heavy Organics Precipitated by varied (v/v) ratios of n-C_5 and n-C_7 Binary Mixtures at 30ml/g of crude oil

Test S/N	Solvent ratio $C_5:C_7$	v/v ratio (ml) $C_5:C_7$	Wt. of crude oil residue (g)	Wt. of HO precipitate (g)	Wt. % of HO ppt.
1	0 : 1	0 : 30	1.0423	0.0101	0.97 ± 0.05
2	1 : 3	7.5 : 22.5	1.0119	0.0169	1.67 ± 0.40
3	1 : 2	10 : 20	1.0126	0.0214	2.11 ± 0.37
4	1 : 1	15 : 15	1.0134	0.0457	4.51 ± 0.65
5	2 : 1	20 : 10	1.0232	0.0217	2.12 ± 0.25
6	3 : 1	22.5: 7.5	1.0367	0.0584	5.63 ± 0.52
7	1 : 0	30 : 0	1.0388	0.1162	11.19 ±0.90

Table 3: Heavy Organics Precipitated by varied (v/v) ratios of n-C_5 and n-C_6 Binary Mixtures at 30ml/g of crude oil

Test S/N	Solvent ratio $C_5:C_6$	v/v ratio (ml) $C_5:C_6$	Wt. of crude oil residue (g)	Wt. of HO precipitate (g)	Wt. % of HO ppt.
1	0 : 1	0 : 30	1.0301	0.0540	5.24 ± 0.32
2	1 : 3	7.5 : 22.5	1.0909	0.0595	5.45 ± 0.57
3	1 : 2	10 : 20	1.0048	0.0586	5.83 ± 1.29
4	1 : 1	15 : 15	1.0280	0.0877	8.53 ± 0.80
5	2 : 1	20 : 10	1.0670	0.0600	5.62 ± 0.57
6	3 : 1	22.5: 7.5	1.0347	0.0886	8.56 ± 0.80
7	1 : 0	30 : 0	1.0388	0.1162	11.19 ± 0.45

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Fig.1: Weight % of HO precipitates vs solvent (v/v) ratios for n-alkane binary mixtures at 30ml total solvent per gram of oil

Fig. 2: Phase diagram for Asphaltene precipitation in Binary mixture of n-alkane solvents at different ratios

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REFERENCES

Branco, V. A. M., Mansoori, G. A., De Almeida Xavier, L. C., Park, S. J. and Manafi, H., 2001, "Asphaltene flocculation and collapse from petroleum fluids", Journal of Petroleum Science and Engineering, 32, pp. 217–230.

Chapman, W. G, Creek, J., Hirasaki, G. J., and Gonzalez, D. L., 2007, "Modeling of Asphaltene Precipitation Due to Changes in Composition Using the Perturbed Chain Statistical Associating Fluid Theory Equation of State", Energy and Fuels, 2, pp. 1231-1242.

Chukwu, O. C., Ofodile, S. E. and Okoye, I. P., 2011, "The Effect of Different Solvent Polarity on the Precipitation of Heavy Organics from a crude oil deposit in the Niger Delta"., Scientia Africana, 10 (2) pp. 9-15.

Chung, F., Sarthi, P. and Jones, R., 1991, "Modeling of Asphaltene and Wax Precipitation", Topical Report, NIPER-498, U.S. Dept. of Energy.

Dubey, S.T., Waxman, M.H., 1995, "Asphaltene adsorption and desorption from mineral surfaces", SPE Reservoir Engineering Journal, pp. 389–395.

Eduardo, B. G., Carlos, L. G., Alejandro, G. V. and Jianzhong, W., 2004, "Asphaltene Precipitation in Crude Oils: Theory and Experiments", Journal of AIChE, 50(10) pp. 2552-2570.

Escobedo, J. and Mansoori, G. A., 1992, "Viscometric principles of onsets of colloidal asphaltene flocculation in paraffinic oils and asphaltene micellization in aromatics", SPE Production, pp 116–122.

Hirschberg, A., Dejong, N. J., Schipper, B. A., and Meijer, J. G., 1984, "Influence of Temperature and Pressure on Asphaltene Flocculation", Society of Petroleum Engineering Journal, 24, pp. 283-291.

Hu, Y. F., Li, S., Liu, N., Chu, Y. P., Park, S. J., Mansoori, G. A., Guo, T. M., 2004, "Measurement and Corresponding States Modelling of Asphaltenes Precipitation", Journal of Petroleum Science and Engineering, 41, pp. 199 – 212.

Kokal, S. L., Najman J., Sayegh S. G. and George, A. E., 1992, "Measurement and Correlation of Asphaltene Precipitation from Heavy Oils by Gas Injection", Journal of Petroleum Technology, 31, pp. 24.

Mansoori, G. A. 1997, "Modeling of asphaltene and other heavy organics depositions", Journal of Petroleum Science and Engineering, 17, pp.101–111.

Mansoori, G.A., Vazquez, D. and Shariaty-Niassar, M., 2007, "Polydispersity of heavy organics in crude oils and their role in oil well fouling", Journal of Petroleum Science and Engineering, 58, (3), pp. 375–390.

Mullins, O., Sabbah, H., Eyssautier, J., Pomerantz, A., Barre, L., Andrews, B., Ruiz Morales, Y., Mostowfi, M., McFarlane, R., Goual, L., Lepkowicz, R., Cooper, T., Orbulescu, J., Leblanc, R., Edwards, J., Zare, R., 2012, "Advances in Asphaltene Science and the Yen-Mullins Model", Energy & Fuels, 26, pp. 3986– 4003.

Pacheco-Sanchez, J. H. and Mansoori, G. A., 1997, "In Situ Remediation of Heavy Organic Deposits Using Aromatic Solvents", SPE Paper No 38966.

Rassamdana, H, and Sahimi, M., 1996, "Asphaltene Flocculation and Deposition: Onset of Precipitation", Alchemy Journal, 42, pp. 3318.

Saraji, S., Goual, L., Piri, M., 2013, "Dynamic Adsorption of Asphaltenes on Quartz and Calcite Packs in the Presence of Brine Films, Colloids and Surfaces", Physicochemical Engineering Aspects, 434, pp. 260-267.

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