Solvent Composition Effect on Cloud and Pour Points of Synthetic Oil and Antan Crude Oil Distillate

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ABSTRACT
This research work investigated the effect of change in composition of crude oil distillate (350-500^{0}C AET) and model synthetic oil, made up of a mixture of Paraffin wax, Methyl Ethyl Ketone (MEK) and Toluene, on the properties of wax precipitation – Cloud point (CP) and Pour point (PP). 1:1 (v/v) ratios of binary mixtures of selected n-alkanes were added to the synthetic oil and crude distillate to alter the compositions. Various ratios of oil/n-alkane mixtures were used at a fixed total volume of 40mls. The results obtained show that the synthetic oil and distillate without the addition of n-alkane solvents, gave Cloud point (CP) and Pour point (PP) values of 21.0^{0}C and 18.0^{0}C / 27.9^{0}C and 10.2^{0}C respectively. On addition of binary n-alkane mixtures (C_7:C_{12}, C_6:C_7, C_6:C_{12}), a lowering of the Cloud point and Pour point relative to the synthetic oil and the distillate was observed as the oil/n-alkane ratios changed. For the Pour point of the crude distillate mixed with C_6:C_7, a steady curvature was observed while with C_7:C_{12} and C_6:C_{12} mixtures, a steady linear decrease to the 1:1 ratio was seen from which a sharp decline then occurred. The experimental investigations shows that the lower the total percentage of n-alkane volume to the oil volume, the greater the tendency to precipitate wax and also that the cloud and pour points of oils decrease with decreasing carbon number of n-alkane solvents.

Keywords: *Waxy crude; Wax precipitation, Binary Mixtures.*

INTRODUCTION

Precipitation is said to be the creation of a solid in a solution when a chemical reaction takes place. The solid created from this chemical reaction (precipitation) is called the precipitate, while precipitant refers to the substance that aids the creation or formation of the solid. [1]

Crude oil is a multicomponent mixture that consists of naturally occurring hydrocarbons, together with organic compounds of sulphur, nitrogen and oxygen, as well as trace amounts of metallic constituents such as vanadium (V), iron (Fe) and nickel (Ni). [2][3][4] The agglomeration, flocculation, precipitation of waxes in crude oil and its untimely deposition on reservoir and subsea pipelines could be said to be one of the major unsolved complex systems/problems encountered by petroleum and natural gas industries when petroleum is extracted, exploited and transported on land, offshore and in deep water offshore. [5][6]

The economic implications of this problem are astronomical. Some well-known harmful effects include: reservoir damage; reduction of the well productivity, that is, the effective flow area of the pipeline is reduced, increasing friction which would ultimately lead to a complete shutdown of oil wells. [7]

The financial strain caused by this problem can lead to the operator of a particular field with which it happens abandoning such a field when it is no longer economical due to the blockage of the facilities by the wax deposits. The U.S Minerals management service published 51 severe plugs related to waxes in Gulf of Mexico flow lines between the years 1992 and 2002 while UK LASMO abandoned the platform with which it operated in November, 1994 because wax blockage kept on re-occurring. [6]

Laboratory determination of cloud points and pour points of crude oil using individual n-alkanes has produced results which give an insight to comprehending the deposition mechanism and the tendency of waxes to precipitate. [8][9]

In this study, determination of the cloud and pour points of a model synthetic oil and crude oil distillate from the Niger Delta region by adding 1:1 binary mixtures of different normal alkane solvents (Hexane, Heptane and Dodecane) has been investigated.

MATERIALS AND METHODS

The following materials were used: Antan Crude Oil Distillate (350-500^{0}C AET) was obtained from the Research and Development Division of the Nigerian National Petroleum Corporation (NNPC), Paraffin wax (58-60^{0}C), n-hexane, n-heptane, n-dodecane, methyl ethyl ketone (MEK), toluene, cloud and pour point tester model-SYD-510D, graduated measuring cylinders (25mls, 50mls, 100mls), corks, beakers, electronic analytical balance model-Radwag AS220/C/2, test tubes, thermometer, sample containers, hand gloves and Water bath model-RE300DB.

The determination of cloud and pour points was done using modified ASTM/IP methods. 5g of wax completely dissolved in a 1:1(w/w) mixture of Methyl ethyl ketone (MEK) and Toluene (ASTM D3235) [10] was poured into a test jar to the level mark (40mls). 40mls of Antan crude distillate was also poured into a test jar to the level mark. The jars were closed tightly by the corks carrying the thermometers and heated (60^{0}C), then placed in an automatic cloud and pour point tester (ASTM D2500, D97). [11][12] Furthermore, 40mls of the synthetic oil/solvent and distillate/solvent mixture was made. The solvents which were different n-alkane mixtures were added in a 1:1 ratio. The jars containing these oil/solvent mixtures were placed in a cloud and pour point tester and the various readings taken.

RESULTS AND DISCUSSION

The cloud and pour points of the model synthetic oil and crude distillate mixed with 1:1 (v/v) ratios of binary mixtures of n-alkane solvents are presented in the tables below:

Table 1: Cloud Points of Model Oil and Crude Distillate with Binary Mixtures of C_6:C_7, C_6:C_{12}, C_7:C_{12}

Test (S/N)	Vol. Ratio (mls)	$C_6:C_7$		$C_6:C_{12}$		$C_7:C_{12}$	
		Model Oil ℃)	Crude Distillate (℃)	Model Oil ℃)	Crude Distillate (℃)	Model Oil ℃)	Crude Distillate (℃)
1	40:0	21.0	27.9	21.0	27.9	21.0	27.9
2	35:5	12.0	16.8	15.3	18.4	17.0	21.4

3	30:10	7.0	11.2	10.9	13.5	14.0	15.4
4	25:15	1.0	2.3	7.0	7.6	10.0	9.7
5	20:20	-4.0	-7.2	2.0	2.3	5.0	5.0
6	15:25	-7.0	-13.7	-3.0	-3.9	2.1	2.4
7	10:30	-12.0	-22.4	-7.0	-14.8	-4.0	-8.4
8	5:35	-14.0	-27.9	-9.0	-19.9	-7.0	-13.9

Table 2: Pour Points of Model Oil and Crude Distillate with Binary Mixtures of C_6:C_7, C_6:C_{12}, C_7:C_{12}

Test (S/N)	Vol. Ratio (mls)	$C_6: C_7$		$C_6: C_{12}$		$C_7: C_{12}$	
		Model Oil (℃)	Crude Distillate (℃)	Model Oil (℃)	Crude Distillate (℃)	Model Oil (℃)	Crude Distillate (℃)
1	40:0	18.0	10.2	18.0	10.2	18.0	10.2
2	35:5	9.9	5.5	13.0	7.4	15.1	8.8
3	30:10	4.1	3.1	9.1	5.6	12.1	6.0
4	25:15	-1.0	-5.8	5.0	2.9	8.0	4.9
5	20:20	-6.0	-14.8	0.0	0.1	3.0	2.6
6	15:25	-10.0	-23.7	-5.0	-12.8	0.0	0.1
7	10:30	-14.0	-41.6	-9.0	-34.0	-6.0	-26.9
8	5:35	-17.0	-65.8	-12.1	-47.5	-10.0	-39.7

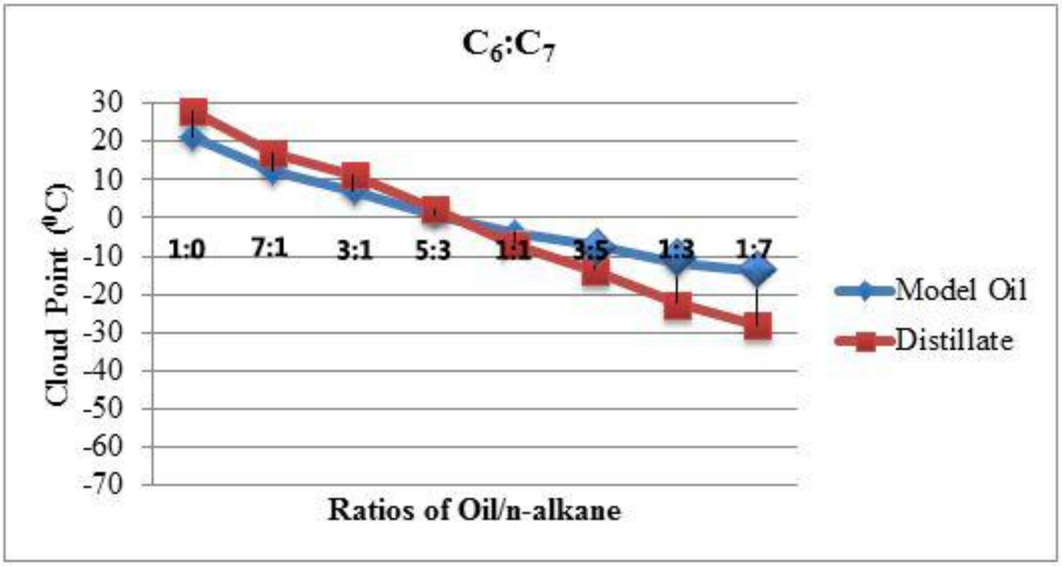

Figure1: Cloud Points of Model Oil and Crude Distillate versus ratios of Binary Mixtures of C_6:C_7

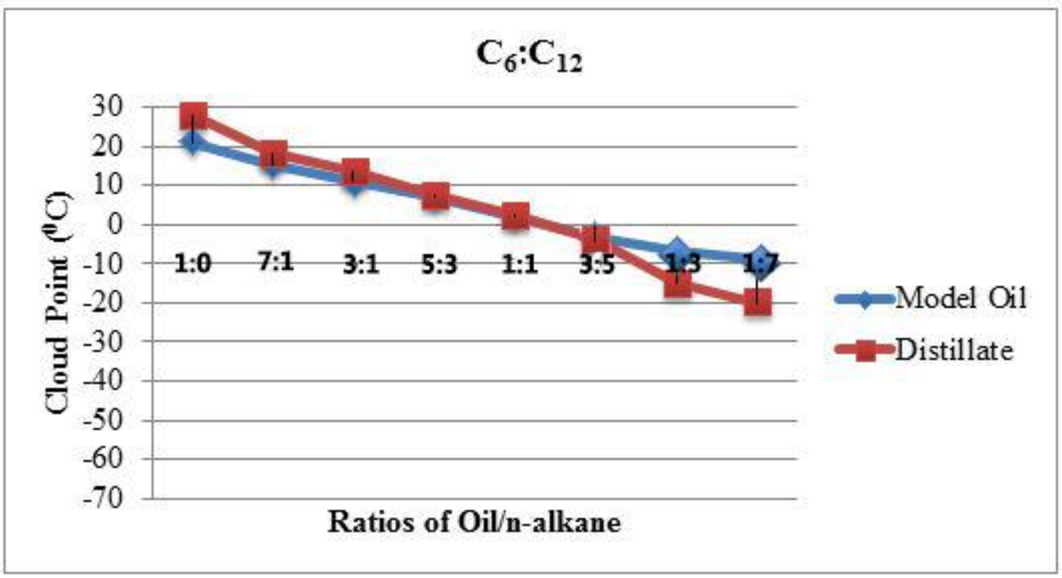

Figure 2: Cloud Points of Model Oil and Crude Distillate versus ratios of Binary Mixtures of C_6:C_{12}

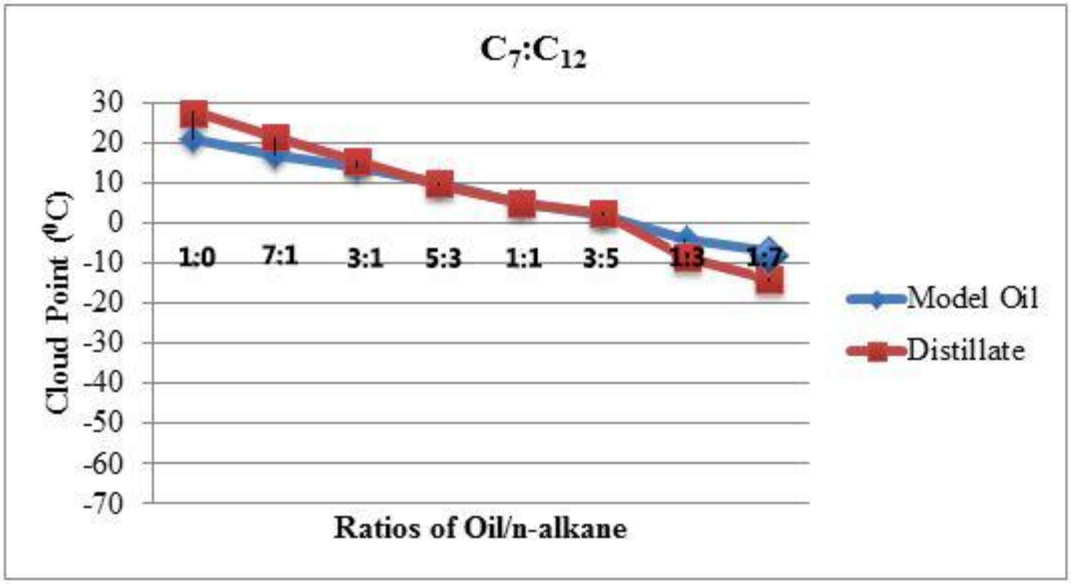

Figure 3: Cloud Points of Model Oil and Crude Distillate versus ratios of Binary Mixtures of C_7:C_{12}

The effectiveness of an additive to reduce or inhibit wax precipitation and deposition is often assessed by the reduction of the cloud and pour points of petroleum fluid. [13] Table 1 presents the result of the cloud points of the model waxy oil and crude oil distillate. Figures 1 to 3 graphically show the reduction effect of the addition of 1:1 (v/v) ratio of n-alkane solvents on the model waxy oil and crude distillate.

In general, the effects of adding these binary mixtures of n-alkane solvents on the cloud point of the model oil and distillate is sensitive to dosage, decreasing the cloud point of the model waxy oil and distillate as concentration increased. A run through the tables and figures indicated earlier show that the decrease in cloud point followed the trend; C_6:C_7 > C_6:C_{12} > C_7:C_{12}. This could be due to the increased solubility of light n-alkane hydrocarbons (C_6 and C_7). Solubility decreases with increase in carbon number of n-alkanes.

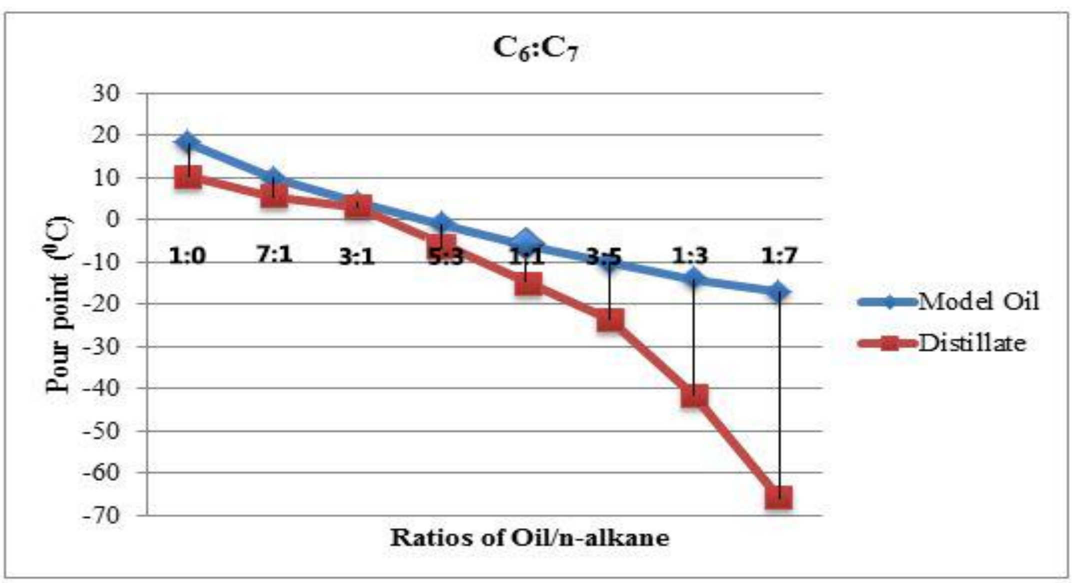

Figure 4: Pour Points of Model Oil and Crude Distillate versus ratios of Binary Mixtures of C_6:C_7

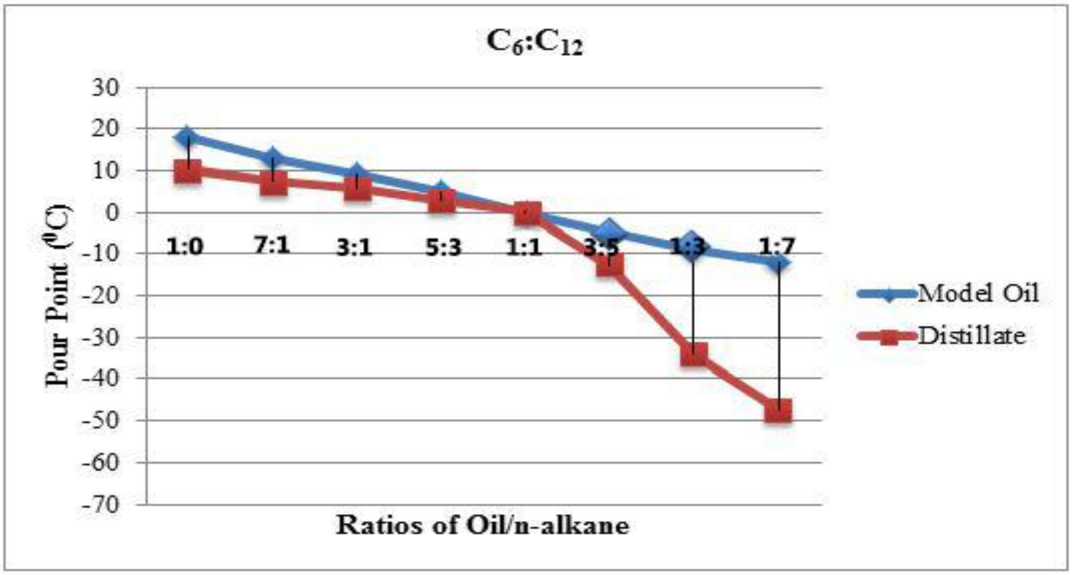

Figure 5: Pour Points of Model Oil and Crude Distillate versus ratios of Binary Mixtures of C_6:C_{12}

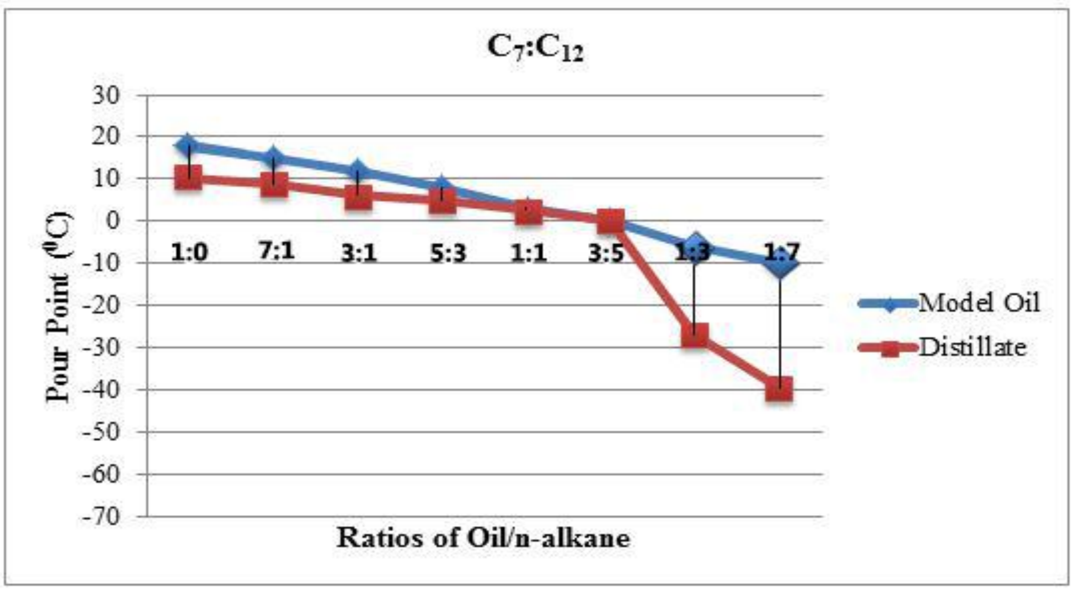

Figure 6: Pour Points of Model Oil and Crude Distillate versus ratios of Binary Mixtures of C_7:C_{12}

Table 2 and Figures 4 to 6 show the data and graphical representation of Pour points of the model waxy oil and crude oil distillate when mixed with binary mixtures of n-alkane solvents at the same concentration as those of the cloud points. From these tables and figures, it is seen that the addition of these binary n-alkane mixtures reduced the pour point temperatures as it did the cloud points. Using the model oil/solvent ratio of 5:35, it is seen that the C_6:C_7 binary mixture gave the lowest pour point at -17^{0}C, followed by C_6:C_{12} whose value was -12^{0}C and the C_7:C_{12}

with -10^{0}C. The Distillate/solvent ratio also followed the same trend with C_6:C_7 binary mixture giving the lowest pour point at -65.8^{0}C, C_6:C_{12} with -47.5^{0}C and C_7:C_{12} with -39.7^{0}C.
The decrease observed in the pour points may be explained by the ability of the n-alkane solvents to introduce strong interaction with the wax crystals, modifying their crystal structure and forming smaller crystals. This in turn reduces the probability of agglomeration of wax crystals, thereby decreasing the pour point. A look at figures 4 to 6 reveals a steady curvature for the pour point of the crude distillate when mixed with C_6:C_7 while with C_7:C_{12} and C_6:C_{12} mixtures, a steady linear decrease to the 1:1 ratio was seen from which a sharp decline then occurred.

CONCLUSION

The experimental results demonstrate that the addition of the selected binary mixtures of n-alkanes to a petroleum fluid may cause a reduction in the cloud and pour points. Binary mixtures of light n-alkanes such as (C_6:C_7) had more pronounced effect by reducing the cloud and pour points of the oils to a greater extent than (C_7:C_{12} and (C_6:C_{12}) mixtures. Normal alkanes were seen to be good solvents for waxes. Two crude oils were seen to not respond the same way to the introduction of large quantities of n-alkanes – especially the high molecular weight solvents. The lower the total percentage of n-alkane volume to the oil volume, the greater the tendency of the oil to precipitate wax. The cloud and pour points of oils decrease with decreasing carbon number of normal alkane solvents.

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