EFFECT OF FLOW IMPROVER BLENDS ON CRUDE OIL RHEOLOGY

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Abstract: Arterial blockage in the petroleum industry is mostly due to the deposition of heavy organics like wax from petroleum fluids. Wax is an undesirable constituent in crude oil due to high pour points and high viscosity index. De-waxing operation is broadly classified into two types namely: one with the use of solvents and other without solvents. In this work, xylene, n-hexane, kerosene and triethanolamine (TEA) were used for de-waxing operation. Different percentages of these solvents were added to the crude oil sample and their effect on the crude oil flow properties was evaluated. All these solvents evaluated improved the flow property of crude oil. Kerosene and triethanolamine (TEA) blends was more effective than the other solvents.

Keywords: Blends, crude oil,pour point, rheology, *Triethanolamine* (TEA), Xylene

Introduction

The demand for crude oil is increasing daily worldwide. This is due to its importance as the world's major source of energy and as the raw material for the manufacture of a wide variety of products for daily living. Industries like agro-allied, refining, petrochemical and textile to mention but few depend on oil. In 2008, oil provided about 34% of the world's energy needs, and oil is expected to continue to provide a leading component of the world's energy mix (Natural Resources Canada, 2010). Petrowiki (2015) described crude oil as a complex mixture of hydrocarbon produced in liquid form, which consist of a large number of petroleum compounds mixed together. These compounds are composed of hydrogen and carbon in various ways and proportions. Each compound is made up of different portions of the two elements. Rarely are two crude oils found that are identical and certainly never are two crude oils made up of the same proportions of the various compounds. These petroleum compounds are Paraffins and Asphaltenes.

Paraffins are relatively high molecular weight. Asphaltenes are very high weight polycyclic aromatic molecules; held in suspension by surrounding asphaltic, resins (maltenes). Whenever there is changes in the environmental condition of the area where the crude oil is been found, each petroleum compounds contained will be affected. For instance, alkanes are deposited as solid (wax) when temperature drops below the cloud point for the particular crude oil. Asphaltenes are also deposited whenever there is reduction in the temperature or pressure or by destabilizing factors that act on the resins such as contact with acid, CO_2 or aliphatic solvents (Petrowiki, 2015). According to Ajienka & Ikoku (1997), the deposition of these waxes affects the flow of the crude oil and its production. In order to control this deposition to improve the flow and production of the crude oil, the rheological properties of this crude oil such as pour point, viscosity and APIg need to be changed and this can be achieved by adding solvents. The common solvents that can be added to improve crude oil flow properties are: xylene, n-hexane, kerosene, and triethanolamine (TEA). Additions of these solvents to crude oil will reduce the wax concentration in the crude oil and improve the flow of the crude oil.

Xylene is an aromatic hydrocarbon mixture consisting of a benzene ring with two methyl groups at various substituted positions. It is a colourless, sweet-smelling major petrochemical produced by catalytic reforming and also by coal carbonization in the manufacture of coke fuel. Xylene is a frequent component of paraffin solvents, used when the tubing becomes clogged with paraffin wax (Kandyala *et al.*, 2010). According to Agency for Toxic Substances and Disease Registry (2015), n-hexane is a chemical made from crude oil. Pure n-Hexane is a colourless liquid, odourless, with boiling points between 50^{o}C and 70^{o}C. It is highly flammable, and its vapours can be explosive. It is widely used as cheap, relatively safe, and easily evaporated non-polar solvent. Most of the n-hexane used in industry is mixed with similar solvents. Kerosene, according to Wikipedia (2015), is a thin, clear liquid formed from hydrocarbon obtained from the fractional distillation of crude oil between 150^{o}C and 275^{o}C. It has the flash point between 37^{o}C and 65^{o}C, auto-ignition temperature of 220^{o}C and its pour point depends on grade, with commercial aviation fuel standardized at – 47^{o}C. As a petroleum product miscible with many industrial liquids, it is used as an additive in diesel fuel to prevent gelling and waxing in cold temperatures.

Triethanolamine (TEA) is a part of a class of organic compounds called ethanolamines; combines the properties of amines and alcohols. It is a viscous organic compound that is both tertiary amine and triol (with three alcohol groups) (IARC, 2012). It is a weak base, colourless and has a mild ammoniacal odour. TEA has molecular formular $C_6H_{15}NO_3$ with relative molecular mass of 149.19, boiling point of 335.4^{o}C, melting point of 20.5^{o}C, density of 1.1242 g/cm^3 at 20^{o}C, vapour pressure less than 1.3 pa at 20^{o}C (DOW, 2010). It is miscible with water, acetone, ethanol and methanol; soluble in chloroform and slightly soluble in benzene, diethyl ether and lignans (Lide & Milne, 1996). TEA is produced from the reaction of ethylene oxide with aqueous ammonia. It is used primarily as an emulsifier and surfactant. It is a common ingredient in formulations used for both industrial and consumer products. The triethanolamine neutralizes fatty acids, adjusts and buffers the pH and solubilises oil and other ingredients that are not completely soluble in water (Popoola *et al.*, 2015). It reacts with acids to form salt and soap and is also used as flow improver additive in crude oil (DOW, 2010). Viscosity reduction is imminent to improve mobility of heavy crude oils; doping with solvent like triethanolamine (TEA), which keeps the wax in solution, is essential in ensuring oil mobility. Based on evaluation of preliminary studies, Taiwo *et al*., (2012), showed triethanolamine (TEA) to be a very good wax deposition inhibitor.

Taiwo *et al*. (2012) described waxy crude oils to have undesirably high pour points and are difficult to handle where the flowing and ambient temperatures are below or less than the pour point. High wax content in crude oil is a threat to the

pipeline transportation of oil from the production wells to the refineries. In previous research works, it has been established that the chemical methods of de-waxing are the most convenient and economical (Akinyemi *et al.,* 2016; Bello *et al.,* 2005; Fadairo *et al.,* 2010; Oseghale *et al.,* 2012). According to Soni *et al.* (2005), the performance of an additive can be determined by its ability to keep the wax components in solution, its ability to attack the wax components and create a barrier for networking of wax particles. This study is aimed at improving the flow of crude oil by reducing its wax content through addition of solvent flow improver blends. The effect of these flow improver blends on the viscosity and pour point of the crude oil was investigated.

Materials and Methods

Materials

The materials used for this study were: crude oil samples, xylene, n-hexane, kerosene, triethanolamine (TEA), pour point test equipment (Herzog MC 850), viscometer (Model 35), water bath, thermometer, thermostat and heater. The reagents used were analytical grade of BDH Chemical Ltd, Poole, England. All crude oil samples used in this study were from Niger-Delta oil field in Nigeria, with density of 847 – 869 kg/m^{3}and American Petroleum Institute gravity (APIg) in the range of 24.4 – 36.5 at 15^{o}C.

Methods

Effectiveness of xylene, n-hexane, kerosene, triethanolamine (TEA) and their blends as flow improvers for crude oils was determined through the pour point test and kinematic viscosity. Each improver, xylene, n-hexane, kerosene and triethanolamine (1% by volume) was added at room temperature (28^{o}C) to the crude oil. Each blend contains the following proportions; blend 1 is a mixture 0.5 ml of xylene and 0.5 ml of n-hexane, blend 2 contains 0.5 ml of triethanolamine and 0.5 ml of kerosene), and blend 3 is a mixture of 0.5 ml of xylene, 0.5 ml of n-hexane and 0.5 ml of triethanolamine. Each blend was added to the crude oil at room temperature (28^{o}C).

Analytical methods

Determination of viscosity

The viscosity was determined using the procedure described by Taiwo *et al.* (2012). The sample was heated to 45^{o}C to improve the fluidity and then allowed to cool to room temperature. The water bath was switched on and the thermostat was set to room temperature (28^{o}C) and inserted into the water bath to regulate the temperature of the water bath. Crude oil sample (50 ml) was poured into the viscometer at room temperature and clasped/fastened onto a metal stand. This was inserted into the water bath with the stand suspended in the water bath cover. The crude oil, with the aid of a sucker pipette was sucked to a set mark in the viscometer. The stop clock was started and the time at which the crude oil flew from the upper mark to the lower mark was recorded. The thermostat was set to 35^{o}C, which automatically started the heater in the water bath raising the temperature to 35^{o}C. The procedures were repeated for temperatures 45^{o}C, 55^{o}C, and 65^{o}C for crude oil samples without adding any improver, with 0.5 ml of improvers – xylene, n-hexane, kerosene and triethanolamine (TEA), and then with the blends (0.5 ml of xylene and 0.5 ml of n-hexane, 0.5 ml of kerosene and 0.5 ml of triethanolamine, 0.5 ml of xylene, 0.5 ml of n-hexane and 0.5 ml of triethanolamine).

Determination of pour points

The equipment used to determine the pour points were: standard pour point test apparatus (Herzog MC 850), thermometer, test tubes and heater. The standard pour point was determined as described by Soni *et al.* (2005). All the samples were heated to 35^{o}C to 40^{o}C and then cooled down to its pour point inside the pour point test apparatus. The samples were checked at regular intervals until flow ceased. If the flow did not occur after 5 seconds when the test tube was tipped horizontally, the temperature was then taken and recorded to give the pour point.

Statistical analysis

Means and standard deviations from means were calculated for each of the analysis results. Data were subjected to analysis of variance in completely randomized design using Statistical Package for Social Science (SPSS) software (version 15, 2007). The calculated mean values were separated using Duncan's multiple range test with significance level of $p<0.05$ (Steel & Torrie, 1980).

Results and Discussion

The viscosities of the crude oil sample at different temperatures are shown in Table 1, while the effect of added flow improvers on the viscosity and pour point of the crude oil at different temperatures is detailed in Tables 2 and 3.

Table 1: The kinematics viscosities of crude oil

Temperature (^{o}C)	Time(s)	Kinematic viscosity (centistokes)
28	1835	54.32
35	381	11.28
45	305	9.03
55	258	7.64
65	222	6.57

Kinematic viscosity (K) = ct, where c= constant = 0.02959, t = time

Effect of added flow improvers on the crude oil viscosity

Table 2 and Fig. 1 show how effective the added flow improvers are on the viscosity of the crude oil as well as their blends. At room temperature (28^{o}C), the kinematic viscosity of the crude oil reduced from 54.32 cSt to 9.32 cSt for the crude oil containing xylene, reduced to 8.79 cSt for crude oil containing n-hexane, reduced to 18.53 cSt for crude oil containing kerosene and reduce to 26.17 cSt for crude oil containing triethanolamine. On adding flow improver blends, blend 1 (mixture of 0.5 ml xylene and 0.5 ml n-hexane), blend 2 (mixture of 0.5 ml trithanolamine and 0.5 ml kerosene) and blend 3 (mixture of 0.5 ml xylene, 0.5 ml n-hexane and 0.5 ml triethanolamine) to the pure crude oil, the viscosity of the crude oil at room temperature reduced. Blend 1 reduced the viscosity from 54.32 cSt to 17.08 cSt, blend 2 reduced it to 20.60 cSt and blend 3 increased it from 54.32 cSt to 60.53 cSt.

Table 2: Viscosities of crude oil and the various blends of crude oils and improvers

Additives (%)	Viscosity (cSt)				
	at 28°C	at 35°C	at 45°C	at 55°C	at 65°C
Crude Oil + 0% flow Improver	54.32±0.03^{b}	11.98±0.01^{b}	9.03±0.03^{a}	7.64±0.01^{a}	6.57±0.01^{a}
Crude Oil + 1% xylene	9.32±0.03^{g}	8.61±0.01^{g}	6.96±0.01^{f}	6.01±0. 01^{d}	5.34±0.01^{e}
Crude Oil + 1% n-hexane	8.79±0.01^{h}	7.62±0.03^{h}	6.90±0.01^{g}	6.01±0.03^{d}	5.62±0.01^{d}
Crude Oil + 1% kerosene	18.53±0.01^{e}	16.52±0.01^{a}	7.49±0.01^{c}	5.87±0.01^{f}	5.32±0.01^{e}
Crude Oil + 1% TEA	26.17±0.01^{c}	10.26±0.01^{e}	7.30±0.01^{e}	5.92±0.01^{e}	4.72±0.01^{f}
Crude Oil + 1% xylene + 1% n-hexane	17.08±0.01^{f}	10.52±0.01^{c}	8.08±0.01^{b}	7.37±0.01^{b}	6.16±0.01^{c}
Crude Oil + 1% TEA + 1% Kerosene	20.60±0.01^{d}	10.30±0.01^{d}	6.63±0.01^{h}	5.27±0.01^{g}	4.29±0.01^{g}
Crude Oil + 1% xylene + 1% n-hexane + 1% TEA	60.53±0.01^{a}	9.86±0.01^{f}	7.43±0.01^{d}	7.22±0.01^{c}	6.51±0.01^{b}

Values are means ± standard deviation replicates scores. Means within a column with different superscript were significantly different ($p < 0.05$)

As temperature increased, the viscosity of the crude oil reduced (Fig. 1). This is in line with the reports by Soni, *et al.* (2005), that crude oil response differently with the same additive at different temperature due to the changes in rheological properties of the crude oil. The Table 2 shows that the additive plays an important role in affecting the viscosity of the crude oil. The viscosity of the crude oil can be improved by adding requisite amount of flow improver, the appropriate volume of the additive has to be added for effectiveness. Triethanolamine (TEA) performs very well at 65°C with 1% volume and agreed with Taiwo*et al.* (2012) report that triethanolamine (TEA) is a very good wax deposition inhibitor. The reduction of viscosity on the addition of these solvents is due to the dissolution of paraffin wax, which shows the effectiveness of these additives.

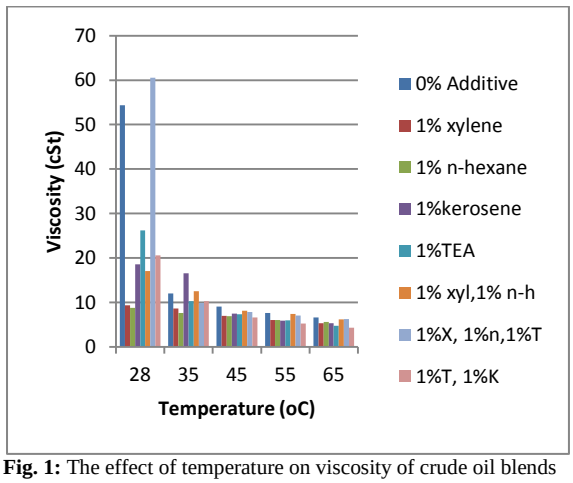

Fig. 1: The effect of temperature on viscosity of crude oil blends

Effect of temperature on the crude oil viscosity

Temperature has a strong effect on viscosity of the crude oil. The kinematic viscosity decreased considerably with increasing temperature (Table 2). At room temperature (28°C) the kinematic viscosity of the crude oil decreased on adding 1% (0.5 ml) of xylene from 54.32 cSt to 9.32 cSt, on adding 1% (0.5 ml) of n-hexane, decreased to 8.79 cSt, decreased to 18.53 cSt on adding kerosene and decreased to 26.17 cSt on adding triethanolamine. But as the temperature increased, the kinematic viscosity decreased considerably. At 35°C, the viscosity decreased from 11.98 cSt to 8.61 cSt for crude oil containing xylene, decreased to 7.82 cSt for crude oil containing n-hexane, decreased to 16.52 cSt for crude containing kerosene and decreased to 10.26 cSt for crude oil containing triethanolamine. At 45°C, the viscosity decreased from 9.03 cSt to 6.96 cSt for crude containing xylene, decreased to 6.90 cSt for crude oil containing n-hexane, decreased to 7.49 cSt for crude oil containing kerosene and decreased to 7.30 cSt for crude oil containing triethanolamine. At 55°C, the viscosity decreased from 7.64 cSt to 6.01 cSt for crude oil containing xylene, decreased to 6.01 cSt for crude oil containing n-hexane, decreased to 5.87 cSt for crude oil containing kerosene and decreased to 5.92cSt for crude oil containing triethanolamine. At 65°C, the viscosity decreased from 6.57 cSt to 5.34 cSt for crude oil containing xylene, decreased to 5.62 cSt for crude oil containing n-hexane, decreased to 5.32 cSt for crude oil containing kerosene and decreased to 4.72 cSt for crude oil containing triethanolamine. On addition of flow improver blends, the viscosity at room temperature reduced from 54.32 cSt to 17.08 cSt (1% xylene and 1% n-hexane), reduced to 20.60 cSt (1% triethanolamine and 1% kerosene) and increased from 54.32 cSt to 60.53 cSt (1% xylene, 1% n-hexane and 1% triethanolamine). At 35°C, the viscosity reduced from 11.98 cSt to 10.52 cSt (1% xylene and 1% n-hexane), reduced 10.30 cSt (1% triethanolamine and 1% kerosene) and reduced 9.85 cSt (1% xylene, 1% n-hexane and 1% triethanolamine). At 45°C, the viscosity reduced from 9.03 cSt to 8.08 cSt (1% xylene and 1% n-hexane), reduced to 6.63 cSt (1% triethanolamine and 1% kerosene) and reduced to 7.43 cSt (1% xylene, 1% n-hexane and 1% triethanolamine). At 55°C, the viscosity reduced from 7.64 cSt to 7.37cSt (1% xylene and 1% n-hexane), 5.27cSt (1% triethanolamine and 1% kerosene) and 7.22 cSt (1% xylene, 1% n-hexane and 1% triethanolamine). At 65°C, the viscosity reduced from 6.57 cSt to 6.36 cSt (1% xylene and 1% n-hexane), reduced to 4.29 cSt (1% triethanolamine and 1% kerosene) and reduced to 6.51 cSt (1% xylene, 1% n-hexane and 1% triethanolamine).

At high temperature wax in the crude oil could not agglomerate and form aggregates, hence reducing the oil viscosity. This is similar to an earlier work of Taiwo *et al.* (2012) on waxy crude oil. The apparent viscosity decreased considerably with increasing temperature. The variation with temperature is attributable to the strong effect of temperature on the viscosity of wax and asphaltene components in the crude oil. At high temperature, the ordered structures of these chemical components are destroyed and hence, reducing oil viscosity (Khan, 1996).

Table 3: Pour point of crude oil sample mixed with different flow improvers

Additives (%)	Pour point (^oC)
Crude Oil + 0% flow improver	32
Crude Oil + 1% xylene	21
Crude Oil + 1% n-hexane	21
Crude Oil + 1% kerosene	16
Crude Oil + 1% TEA	17
Crude Oil + 1% xylene + 1% n-hexane	20
Crude Oil + 1% TEA + 1% kerosene	14

Effect of flow improvers on the pour point

Table 3shows the depression of the pour points of the crude oil. Xylene reduced the pour point of the crude oil up to 21^{o}C from 32^{o}C. n-hexane reduced also the pour point to 21^{o}C while kerosene reduced it to 16^{o}C. Triethanolamine (TEA) reduced the pour point to 17^{o}C, blends of xylene and n-hexane reduced it to 20^{o}C while triethanolamine and kerosene blends reduced it to 14^{o}C.The depression in pour point is mainly due to wax crystal modification. Pour point depressants molecules are adsorbed on the various crystals faces, thereby decreasing the interlocking forces between two nuclei of wax molecules and deforming the regular crystal growth (Bello *et al.*, 2005). The pour point depressant changes the wax crystal shapes when present in crude oil from thin extensively interlocking plates to more compact crystals by co-crystallizing with the wax (Fadairo *et al.*, 2010). The triethanolamine (TEA) actively decreased the pour point of the samples and their wax deposition potentials on doping. The oxygen containing group in the triethanolamine takes the role of inhibiting the growth waxes and poisoning them by adsorptive surface poisoning mechanism (Taiwo *et al.*, 2012). The waxes then occurred in small sized particles in the crude oil and cannot form net-like structure required for solidification and deposition.

Conclusion

Effects of xylene, n-hexane, kerosene and triethanolamine (TEA) on pour point and rheological properties of the crude oil were investigated. All the additives evaluated in this study were effective in depressing the pour point and the flow properties of crude oil. Xylene and n-hexane were more effective than kerosene and triethanolamine at low temperature (28^{o}C, 35^{o}C, 45^{o}C) while kerosene and triethanolamine were more effective than xylene and n-hexane at high temperature (55^{o}C, 65^{o}C). Triethanolamine and kerosene blends were more effective at high temperature (55^{o}C, 65^{o}C) than using triethanolamine and kerosene separately. Blending was effective for combating wax deposition in crude oil. Temperature had significant effect on pour point and viscosity of crude oil and should be considered in choosing appropriate crude oil flow improvers. Increase in temperature decreased viscosity of the crude oil.

References

Agency for Toxic Substances & Disease Registry. 2015. n-Hexane. Available at: http//www.atsdr.cdc.gov/substances/toxsubstance.asp.

Ajienka JA & Ikoku CV. 1997. Waxy crude oil handling in Nigeria: Practices, problems and prospects. *Energy Source*, 12(4): 463 – 478.

Akinyemi PO, Udonne JD, Efeovobokhan VE & Ayoola AA. 2016. A study on the use of plant seed oils, triethanolamine and xylene as flow improvers of Nigerian waxy crude oil. *J. Appl. Res &Techn*., 14: 195 – 205.

Bello OO, Ademodi BT & Akinyemi PO. 2005. Xylene-based inhibitor solves crude oil wax problems in Niger Delta pipeline. *Oil & Gas J.*, 103(10): 56 – 59.

DOW, 2010. Product Safety Assessment: DOW^{TM} Triethanolamine. Available at: www.dow.com/productsafety/finder.

Fadairo A, Ameloko A, Ako C. & Duyilemi A. 2010. Modeling a wax deposition during oil production using a two-phase flash calculation. *Petroleum & Coal*, 52(3): 193 – 202.

IARC, 2012. Triethanolamine. *IARC Monograph*, 77: 381 – 385.

Kandyala R, Raghavendra SP & Rajasekharan ST. 2010. Xylene: An overview of its health hazards and preventive measures. *J. Oral & Maxillofacial Pathology*, 14(1): 1 – 5.

Khan MR 1996. Rheological property of heavy oils and heavy oil emulsions. *Energy Source*,18:385 – 391.

Lide DR. & Milne GWA. 1996. *Properties of Organic Compounds*. Version 5.0. CRC Press, Boca Raton. FL.

Natural Resources Canada. 2010. The Importance of Crude Oil. Available at http://www.nrcan.gc.ca/energy/publications/markets/6505.

Oseghale CI, Akpabio EJ & Edebor O. 2012. Mitigating potential risk of paraffin wax deposition on oil pipelines in Niger Delta. *J. Engr.&Appl. Sci.*, 7(4): 348 – 352.

Petrowiki 2015. Crude Oil Characterization. Available at: http://petrowiki.org/Crude_oil_characterization.

Popoola CA, Ayo JA, Adedeji OE & Ogungbemi A 2015. Triethanolamine (TEA) as Flow Improver for Heavy Crude Oils. *IOSR J. Appl. Chem.(IOSR-JAC)*, 8(1): 34 – 38.

Soni HP, Bharambe DP, Nagar A &Kiranbala, B 2005. Synthesis of chemical additives and their effect on akholjuni crude oil (Gujarat, India). *Indian J. ChemicalTechn.*, 12: 55 – 61.

Steel RGD & Torrie JH. 1980. *Principles and Procedures of Statistics*. A Biometric Approach. 2nd edn, Auckland, New Zealand, McGraw-Hill. pp 345- 357.

Taiwo E, Ololorin J & Afolabi T 2012. Crude oil transportation: Nigerian Niger-Delta Waxy Crude. Crude Oil Exploration in the World; Prof. Mohamad Younes (Ed.). ISSBN: 978-953-51-0379-0. InTech. Available from: http://www.intechopen.com/books/crude-oil-exploration-in-the-world/crude-oil-transportation-nigerian-niger-delta-waxy-crude-oil.

Wikipedia 2015. Kerosene. Available at: http://en.wikipedia.org//wiki/Kerosene.