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Triethanolamine (TEA) As Flow Improver For Heavy Crude Oils

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Abstract: *The production of crude oils is normally in remotes areas and pipelines are the most energy efficient way of transporting it. The crude oils being very viscous on extraction have to go through some processing to enable them to be transported by pipeline. Fresh crude oil is relatively mobile; however at lower temperatures when it has to be transported long distances through pipelines, it gradually becomes thicker and sluggish hampering its flow properties by forming crystals of wax on its wall and making it difficult to pump. Some heavy crude oils are characterized by high viscosity, high content of asphaltenes, low quantity of paraffin components and appreciable amounts of sulphur. Therefore, it is important to minimize the viscosity of the heavy crude oil. One well-known method of alleviating the problem is to treat the crude oil with wax crystal modifier. There are several options available including chemical additives such as flow improvers, viscosity reducer, and pour point depressants (PPDs). This work involves the evaluation of triethanolamine (TEA) as pour point depressant and flow improver by changing the feed ratios. Niger-Delta crude oil was used to evaluate the efficiency of triethanolamine (TEA) as additive through measurements of pour point and viscosity of treated and untreated crude oil. Triethanolamine (TEA) interferes in the wax crystallization process thus modifying the crystal structure of the paraffin present in the crude oil resulting in lowering pour point and viscosity of the crude oil.*

Keywords: *Pour point, Pour point depressants, Viscosity, Flow improver, Asphaltenes, Triethanolamine (TEA),*

I. Introduction

Crude oils are complex hydrocarbon mixtures containing non-polar n-paraffins and polar components such as asphaltenes. Heavy oil is defined as petroleum which has a density equal or lower than 20 API, but if petroleum has 10 API or less, it is considered as extra heavy oil or bitumen, which is denser than water (Khan, 1996). According to some estimates from Inter Energy Agency (IEA), as reported by Atta *et al*. (2013), heavy oil represents at least half of the recoverable oil resources of the world. Crude oil having high wax content causes many problems during production, storage and transportation. One of the main problems is the crystallization and deposition of paraffin wax crystals in the flow line which is more severe in winter (Soni *et al*., 2005). At low temperature, as the crude oil flows through these pipelines, crystals of wax may be formed on its walls. These wax crystals then grow in size until the whole inner wall is covered with wax layers; this result into the reduction of flow and extra burden on the pumping system. As the wax thickness increases, pressure across the pipe needs to be increased to maintain a constant flow rate, thus the power requirement to transport the crude oil also increases. Another major problem during the handling of waxy crude oil as reported by Egyptian Petroleum Research Institute (2006), is restarting of the pipeline after prolong shut down period; the cooled oil slowly develops gel structure which results into high yield stress.

The wax crystals deposition leads to higher viscosity of crude oil and reduction of the effective cross-sectional area of the pipe (Anons, 2013). Solving the wax deposition problems is therefore an economically beneficial target which can be highly achieved by introducing chemical additive to the crude oil in order to reduce its viscosity and pour point temperature. Although crude oil treatment with chemical additives is not the only known solution for inhibition of wax deposition, it remains the preferred solution over other options like pigging, heating and biological treatments (Atta *et al.*, 2013). The pour point and rheological properties of the crude oil can be improved by adding requisite amount of flow improver. Johnston *et al.* (2009) described flow improvers or pour point depressants (also known as drag-reducing agents, DRAs) as long-chain, ultra-high-molecular-weight that reduces the level of turbulence in fluid streams. They are generally used to lower the pour point, viscosity, yield stress of the crude oil and improve the fluidity of waxy crude oil, thereby reduce the extra pumping cost.

According to Johnston *et al*. (2009), typical molecular weights for drag-reducing polymers are greater than 5million and when using parts per million (ppm), concentration level in the fluid stream, drag-reducing polymers interact with the fluid molecules that reduce the formation and propagation of turbulent eddies. It was explained that this decreases deviations in velocity relative to the bulk flow of fluid, causing the hydraulic energy to be more focused on moving the fluid stream down the pipeline rather than in a chaotic random motion and the reduced frictional pressure losses enable pipeline operators to lower operating pressure or increase the rate of fluid flow.

Viscosity is the ratio of shear stress to shear rate. It is defined empirically as the resistance offered by fluid to flow at a given temperature. An increase in temperature of the oil lowers the viscosity, while a decrease in temperature increases the viscosity. The viscosity-temperature relationship must be established accurately in order to determine pump ability of the oil.

Pour point is the temperature at which the crude oil is just able to flow and below which there is complete absence of flow in it. It represents the lowest temperature at which the crude oil can be stored or handled without congealing in the tanks or pipelines.

According to Ajienka (1997), pour point is usually 10^0C – 20^0C lower than cloud point. Cloud point is defined as the temperature at which the first wax crystal separates out from crude oil. Below the cloud point, crude oil containing high amount of wax possesses high pour point and exhibit non-Newtonian viscosity behavior. The wax appearance temperature (WAT) and the pour point temperature (PPT) are good pointers to the temperature regime, in which a waxy crude oil is expected to start to show non-Newtonian behavior as reported by Taiwo, *et al.* (2012). As temperature decreases, the abrupt rise in crude oil viscosity depends upon the quantity as well as type of wax present in it.

Soni *et al.* (2006) discussed the synthesis and evaluation of polymeric additives as pour point depressants and flow improvers for crude oil. They studied the rheological properties of crude oil (with or without additives) in terms of shear rate, shear stress, yield stress and viscosity and listed three main characteristics for any additive to behave as flow improver should have, which are:

(i) A wax like paraffin part, typically mixture of linear alkyl chain of 14 to 25 carbon atoms long that co-crystallize with "oils" wax forming component.
(ii) A polar component typically acrylates or acetates that limits the degree of co-crystallization.
(iii) Polymers that when adsorbed on the growing wax crystals stearically hindered their growth, resulting into small crystal.

It should be noted that any additive as a pour point depressant may be ineffective to reduce viscosity, yield stress and enhance the flow. The following factors according to Soni *et al.* (2006) play an important role in the efficiency of flow improvers and pour point depressants

- a number of pendant of alkyl side chains and the length and distance between them.
- the solubility of the additives in crude oil which depends on their average molecular weights.
- amorphous and crystalline parts of additive are very important in determining its efficiency
- physical and chemical stability of additive.
- if additive is copolymer then monomer to monomer ration should be taken into consideration.

Triethanolamine (TEA), co-polymer, satisfies most of these requirements. 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 335.4^0C, melting point of 20.5^0C, density of $1.1242g/cm^3$ at 20^0C, vapour pressure less than 1.3pa at 20^0C. 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 P^H and solubilises oil and other ingredients that are not completely soluble in water. 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.* (2003), showed triethanolamine (TEA) to be a very good wax deposition inhibitor.

II. Experimental Methods

Evaluation tests of flow Improvers

Effectiveness of triethanolamine (TEA) as flow improver for the heavy crude oils was determined through the pour point test and kinematic viscosity.

Experimental Materials

The materials used for this study were: crude oil samples and triethanolamine (TEA). 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 API gravity in the range of 24.4 – 36.5 at 15^{0}C. Standard methods were employed in determination of the physical properties.

Determination of pour points

The equipment used to determine pour points were: a standard pour point test apparatus, a thermometer, test tubes and heater. The standard pour point was obtained in all cases with the sample generally heated to about 35^{0}C to 40^{0}C and then cooled down to its pour point inside the pour point test apparatus. The sample was 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.

Determination of Viscosity

The equipment used for viscosity determination includes the following: Viscometer, a water bath, a thermometer, a thermostat and heater. The viscosity was obtained by following this procedure: the sample was heated to about 45^{0}C to improve the fluidity and then allowed to cool to room temperature. While the sample cools, the water bath was switched on with thermometer; thermostat was set to room temperature and inserted into the water bath to regulate the temperature of the water bath. 50ml of the crude oil sample at room temperature was poured into the viscometer 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 time at which the crude oil flows from the upper mark to the lower mark was recorded. The thermostat was set to 35^{0}C, which automatically starts the heater in the water bath raising the temperature to 35^{0}C. The procedures were repeated for temperature 45^{0}C, 55^{0}C, and 65^{0}C for samples with and without triethanolamine (TEA).

III. Results and Discussions

Effect of Added Triethanolamine (TEA) on the Viscosity and Pour point of the heavy Crude oil

The viscosity of the pure crude oil sample at different temperature is shown in Table 1, while the effect of added triethanolamine (TEA) on the viscosity and pour point of the crude oil at different temperatures is detailed in Table 2 and Table 3 respectively below:

Table 1: Viscosity of Pure Crude oil Sample

Temperature (^{0}C)	Time (sec)	K. Viscosity (cSt)
28	1835	54.32
35	381	11.28
45	305	9.03
55	258	7.64
65	222	6.57

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

Table 2: Viscosity of Crude oil Sample mixed with Different percentage of Triethanolamine (TEA) at different Temperatures.

Percent. of Additives(%)	Viscosity at 28^{0}C (cSt)	Viscosity at 35^{0}C (cSt)	Viscosity at 45^{0}C (cSt)	Viscosity at 55^{0}C (cSt)	Viscosity at 65^{0}C (cSt)
Crude Oil + 0% TEA	54.32	11.98	9.03	7.64	6.57
Crude Oil + 0.05% TEA	17.74	9.32	6.21	5.12	4.20
Crude Oil + 0.1% TEA	18.56	9.59	6.30	5.33	4.23
Crude Oil + 0.5% TEA	21.31	9.89	6.93	5.39	4.68
Crude Oil + 1% TEA	26.17	10.26	7.30	5.92	4.72
Crude Oil + 2.5% TEA	31.17	11.19	7.45	6.93	4.89
Crude Oil + 5% TEA	34.75	11.72	7.61	6.99	5.08

Table 3: Pour point of Crude Oil Sample mixed with Different Percentage of Triethanolamine (TEA)

Percentage of Additives (%)	Pour Point (^{0}C)
Crude Oil + 0% TEA	32
Crude Oil + 0.05% TEA	17
Crude Oil + 0.1% TEA	17
Crude Oil + 0.5% TEA	17
Crude Oil + 1% TEA	17
Crude Oil + 2.5% TEA	17
Crude Oil + 5% TEA	17

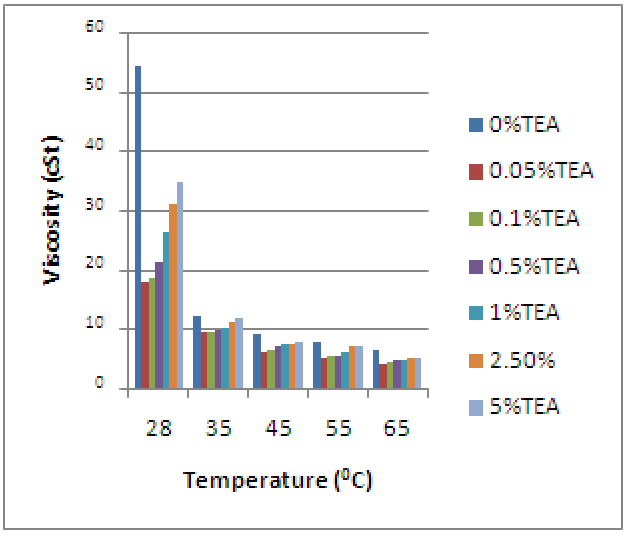

Figure1: Chart of proportions of TEA in crude oil and its viscosity

Effect of Chemical additive on the crude oil viscosity: Table 2 and Figure 1 show the effect of triethanolamine (TEA) on the viscosity of crude oil at different temperature. The effect of chemical additive (TEA) on the viscosity of crude oil was evaluated. Different doses (i.e. 0.05%, 0.1%, 0.5%, 1%, 2.5% and 5%) were tried at different temperatures to determine the viscosity. As can be seen from Table 2, triethanolamine (TEA) decreased the viscosity at different temperatures. As volume of added triethanolamine increases, the viscosity of the crude oil increases and vice versa (Figure 1). This is in line with findings of Soni, *et al.* 2005, in which it was observed that crude oil responses differently with the same additive at different doses, as a result of changes in rheological properties of the crude oil.

The table shows that the molecular weight of the additive plays an important role in affecting the viscosity of the crude oil. The higher molecular weight polymer imparts higher viscosity. The structure of the polymer and its solubility in crude oil are also important. 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^{0}C with 0.05% volume and agreed with Taiwo, *et al.* 2012, report that triethanolamine (TEA) is a very good wax deposition inhibitor. With 0.05% volume fraction of triethanolamine (TEA), the shear thinning behavior is enhanced, and the viscosity as well as the pour point decreases as temperature increases. The reduction of viscosity on the addition of the solvent is due to the dissolution of paraffin wax, which shows the effectiveness of triethanolamine (TEA).

Effect of Temperature on the crude oil viscosity: Temperature has a strong effect on viscosity and viscous behavior. The kinematic viscosity decreases considerably with increasing temperature. From Table 2, 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 decreases 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**).

Effect of Temperature on the pour point: 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. 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. Table 3 shows the depression in pour point. Triethanolamine (TEA) reduced the pour point of the crude oil up to 17^0C from 32^0C. It can be seen from the table that 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. The waxes then occur in small sized particles in the crude oil and cannot form net-like structure required for solidification and deposition.

IV. Conclusion

The resins and asphaltenes present in the crude oil play a significant role on the flow properties of crude oil. In a search for effective chemical additives for improving the flow properties of crude oil, triethanolamine (TEA) was synthesized and characterized in the laboratory and its effects on pour point and rheological properties of the crude oil was investigated. Triethanolamine (TEA) is an effective crude oil pour point depressant and flow improver. It satisfies most of the requirements to act as a pour point depressant and flow improver. It has also been shown that temperature has significant effect on pour point and viscosity of crude oil.

References

[1]. Ajienka, J.A and Ikoku, C.V. (1997). Waxy Crude Oil handling in Nigeria: Practices, Problems and Prospects. Energy Source. 12(4), 463 – 478.

[2]. Anonymous, (2013). Oilfield Drilling and Exploration Chemicals: Pour Point Depressants. www.constol.co.in/pro_oil_ppd.asp. (June 23, 2013).

[3]. Atta, A.M., El-Ghazawy, R.A., Morsy, F.A., Ali, M.S.A. and Elmorsy, A. (2013). Synthesis and Characterization of Polymeric additives and their effect on flow properties of waxy Egyptians Crude Oil. Global Journal of Science Frontier Research Chemistry. 13(10), 21 – 27.

[4]. Castro, L.V., Flores, E., and Vazquez, F., (2012). Terpolymers as Flow Improvers for Mexican Crude Oils.

[5]. DOW, (2010). Product Safety Assessment: DOW™ Triethanolamine.

[6]. Available at: www.dow.com/productsafety/finder.

[7]. Egyptian Petroleum Research Institute (2013). Improvement of Crude Oils Flow Properties through the use of Locally Produced Polymeric Materials.

[8]. IARC, (2012). Triethanolamine. IARC Monograph. 77, 381 – 385.

[9]. Johnston, R.L., Lauzon, P.A. and Pierce, J.D. (2009). Increasing Heavy Crude Oil flow through a New Flow Improver Product – A case study. A report by Conocophillips Specialty Products Inc.

[10]. Khan, M.R. (1996). Rheological property of heavy oils and heavy oil emulsions. Energy Source.18, 385 – 391.

[11]. Lide, D.R. and Milne, G.W.A. (1996). Properties of Organic Compounds. Version 5.0. Boca Raton. FL. CRC Press.

[12]. Soni, H. P. and Bharambe, D.P. (2006). Synthesis and Evaluation of Polymeric Additives as Flow Improvers for Indian Crude Oil. Iranian Polymer Journal. 15(12), 943 – 954. Available online at: http//www.journal.ippi.ac.ir.

[13]. Soni, H. P., Bharambe, D.P., Nagar, A., and Kiranbala (2005). Synthesis of Chemical Additives and their effect on Akholjuni Crude Oil (Gujarat, India). Indian Journal of Chemical Technology. 12, 55 – 61.

[14]. Taiwo, E., Otolorin, J. and 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.