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Performance of Temperature Over Selected Flow Improvers

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Abstract- Wax crystallization and deposition at temperature below wax appearance temperature (WAT) in crude oil stream poses a serious problem, in the production, storage, processing and transport of crude oil. In this attempt, high temperature (heating) which readily comes to mind might not be the best option when its contribution is evaluated side by side with that of triethanolamine(TEA) and ethylvinyleacetate(EVA). This is particularly true when the cost of heat is put into consideration together with its operational difficulties of working at high temperatures. 0%, 0.025%, 0.05%, 0.1%, 0.2%, 0.4% and 1% concentrations (by volume percentage) of TEA and EVA were separately introduced into separate but same quantities of the same crude oil stock at temperatures 30oC, 40oC, 50oC, 60oC, 70oC and viscosity effects monitored with respect to temperatures. Zero concentration of the improvers served as control. TEA and EVA both drastically dropped viscosity of the crude oil very close to what temperature could offer although temperature had an overriding effect. EVA did not appear to be affected by higher temperature/heat as with TEA. Combination of TEA or EVA with higher temperature gave better results as from the lowest viscosity achieved across the temperatures, viz: 0.0944(TEA) and 0.1015 (EVA) which happened at 70oC and concentration of 0.025%. TEA proved to be a better flow improver with lowest viscosity of 0.1124centistokes against EVA having 0.1184 centistokes at 30oC and 0.025% concentration. The same was also observed at the apex temperature of 70oC (TEA = 0.0997, and EVA = 0.1015centistokes at 0.025% concentration). These findings when applied in the industry will minimize the processing cost of crude oil both in material and non-material terms.

Index Terms- Crude oil, triethanolamine, ethylvinylactate, viscosity, temperature, drag reducing agent, flow improver.

I. INTRODUCTION

The search for the best method of solving the flow problem in crude oil is a very beneficial one because of its effects in terms of overhead cost and the concatenation of economic implications owing to the enviable position of crude oil as the world's major energy source for various uses. Crude oils consists of complex mix of hydrocarbons with non-polar n-paraffins and polar components like asphaltenes. Heavy oil are crude oils with densities of 20 API or less, those of 10 API or lower are referred to as extra heavy oil or bitumen, being more dense than water (Khan, 1996). From estimations of International Energy Agency (IEA), which Atta et al. (2013) reported, not less than half of the world's retrievable oil resources are heavy oils. This gives the above flow problem of crude oil prominence.

High level of constituent wax in crude oil brings about challenges in its processes of producing, storing and transport. A major issue at the centre of it all is the crystallization and deposition of crystals of paraffin wax along the flow line being more serious during winter (Soni et al., 2005), as well as through seas and ocean floors. Precipitates of wax generate on the walls of the pipelines during low temperatures. The crystals grow in size and eventually covering the entire walls with layers of wax with a flow reduction and extra demand on the pumping mechanism. With the increased thickness of wax deposits, pumping pressure needs to be raised if the system is to maintain steady rate of flow. This in turn will place extra demand on the power needed for the crude oil transportation. The next serious matter in waxy crude oil handling by Egyptian Petroleum Research Institute (2006), is setting back pipeline into operation after prolong shut down period, may be due maintenance. The oil would have developed gel structure causing high yield stress. The deposited wax crystals results to increased viscosity of crude oil as well reduces the effective cross sectional area of the pipe (Anons, 2013).

Treating the crude oil with chemical additive is an economically viable target solution towards wax deposition to reduce crude oil 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 most preferred solution over other options like pigging, heating and biological treatments (Atta et al., 2013). This is basically due to cost (energy, time, stress and materials) and convenience efficiency, speed and accuracy). Relevant quantities of drag reducing agents in parts per million enhances the pour point and rheological properties of the crude oil. 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. These typically reduce pour point, viscosity, yield stress of crude oil and enhance fluidity of waxy crude oil, thus reduce the extra pumping cost. Transport of crude oil around/ below its pour point needs a deep understanding of crude oil chemistry, its rheological properties, and operating conditions. Optimization of PPD dosages can affect cost savings (Soni and Bharambe, 2006). The practice of identifying, quantifying, and mitigating all the flow risks associated with offshore pipelines and subsea systems is called flow assurance.

Triethanolamine (TEA) co-polymer, is a part of a class of organic compounds called ethanolamines. It 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 substance and has a mild ammoniacal odour.

TEA has molecular formula C6H15NO3 with relative molecular mass of 149.19, boiling point of 335.40C, melting point of 20.5oC, density of 1.1242g/cm3 at 20oC, vapour pressure less than 1.3Pa at 200C. 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. TEA satisfies most of the requirements of flow improvers. Since viscosity reduction is essential to improve mobility of heavy crude oils; doping with solvent like triethanolamine (TEA), which keeps the wax dispersedly suspended 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.

On the other hand, the copolymer of ethylene and vinyl acetate is called Ethylene-vinyl acetate (EVA) or poly (ethylene-vinyl acetate-PEVA). The vinyl acetate weight percent normally ranges between 10 to 40%, and the rest being made up of ethylene. It is almost an elastomeric material in softness and flexibility; though a polymer but may be processed like other thermoplastics. It is a material that is very clear and glossy, low-temperature toughness, resists stress-cracking, hot-melt adhesive waterproof characteristics, and resists UV radiation. EVA is characterized by a distinctive odour of vinegar and competes with rubber and vinyl goods in various electrical applications. Ethylene vinyl acetate (EVA) polymer chains consist of the unit monomers linked through addition of free-radical polymerization reaction via the double bonds of ethylene and vinyl acetate (VA) monomers.

In this work, effect of temperature on the viscosity of crude oil in connection with concentration of TEA and EVA were monitored, compared and analysed. Triethanolamine and ethyl vinyl acetate performances as flow improvers were compared with that of temperature. By subjecting each under the same conditions, where calculated percentages of the improvers were introduced into the crude oil sample and then heating alone, as well as with the improvers crosschecked, the results were used to reveal the variance in performance, and to what extent temperature has influence/edge over the improvers. It also tries to enquire if the improvers alone can conveniently serve as alternative to heating or high temperature in flow assurance. The viscosities are monitored to ascertain the best result and condition for flow improvement.

II. EXPERIMENT

Materials: Separating funnel, Retort Stand, 50ml and higher volume beakers, 25ml, 50ml, 100ml, 1000ml measuring cylinders, Pipette, Thermometer, constant temperature water bath, Viscometer, Pour point apparatus (Manufacturer: Koehler Instr. Co. USA, Model: K46000),

Laboratory Reagents: Raw Crude Oil (Nigerian origin from Alakiri Flow Station- Well 9 OML 18 in Rivers State of Nigeria. Date of collection is 28th April, 2017. It is also worthy of note that this particular crude has not undergone any form of treatment hence it is hereinafter and above referred to as raw crude oil), Triethanolamine, Ethyl Vinyl Acetate,

Methods: The raw crude oil is shaken, kept to settle which separated into layers. It was separated by means of the separating funnel. Calculated quantities in percentage of Triethanolamine (TEA) were introduced into the separate but the same and equal volumes of crude samples in beakers namely: 0.025%, 0.05%, 0.1%, 0.2%, 0.4% and 1%.

They were properly stirred for mixture homogeneity and poured into the viscometer. Its variant behaviour in terms of viscosity with respect to concentrations of TEA was monitored and recorded as in the tables. Each of the same samples above was heated to different temperatures viz: 30oC, 40oC, 50oC, 60oC and 70oC by means of a constant temperature water bath and viscosity recorded. The same process above was repeated using Ethyl vinyl Acetate (EVA) and recorded to evaluate the performance of temperature over the DRAs.

III. RESULTS AND DISCUSSION

1. Results

Table 1: Time and Viscosities of Crude Oil at Different Concentrations (in percentage) of Triethanolamine (TEA) and Temperatures (in degree celsius).

	30^{o}C		40^{o}C		50^{o}C		60^{o}C		70^{o}C	
	Time (s)	Viscosity (Centistokes)	Time(s)	Viscosity (Centistokes)	Time	Viscosity (Centistokes)	Time(s)	Viscosity (Centistokes)	Time(s)	Viscosity (Centistokes)
Raw Crude oil only	9.35	0.2767	5.30	0.1568	4.03	0.1192	3.66	0.1083	3.57	0.1056
Crude Oil + 0.025% TEA	3.80	0.1124	3.65	0.1080	3.55	0.1050	3.48	0.1030	3.37	0.0997
Crude Oil + 0.05% TEA	4.51	0.1335	3.53	0.1045	3.43	0.1015	3.39	0.1003	3.19	0.0944
Crude Oil + 0.1% TEA	5.69	0.1684	4.17	0.1234	3.90	0.1154	3.75	0.1110	3.63	0.1074
Crude Oil + 0.2% TEA	5.97	0.1767	4.40	0.1302	3.92	0.1160	3.82	0.1130	3.72	0.1101
Crude Oil + 0.4% TEA	6.29	0.1861	4.76	0.1408	4.10	0.1213	3.89	0.1151	3.80	0.1124
Crude Oil + 1% TEA	6.61	0.1956	5.02	0.1485	4.39	0.1299	4.08	0.1207	3.92	0.1160

Table 2: Time and Viscosities of Crude Oil at Different Concentrations (in Percentage) of Ethyl vinyl acetate (EVA) and Temperature (in degree Celsius).

	30^{o}C		40^{o}C		50^{o}C		60^{o}C		70^{o}C	
	Time(s)	Viscosity (Centistoks)	Time(s)	Viscosity (Centistokes)	Time(s)	Viscosity (Centistokes)	Time(s)	Viscosity (Centistokes)	Time(s)	Viscosity (Centistokes)
Raw Crude Oil + 0% TEA & EVA	9.35	0.2767	5.30	0.1568	4.03	0.1192	3.66	0.1083	3.57	0.1056
Crude Oil + 0.025% EVA	4.00	0.1184	3.91	0.1157	3.70	0.1095	3.55	0.1050	3.43	0.1015
Crude Oil + 0.05% EVA	4.08	0.1207	3.92	0.1160	3.72	0.1100	3.57	0.1056	3.45	0.1021
Crude Oil + 0.1% EVA	4.10	0.1213	3.94	0.1166	3.76	0.1113	3.60	0.1065	3.48	0.1030
Crude Oil + 0.2% EVA	4.12	0.1219	3.98	0.1178	3.82	0.1130	3.62	0.1071	3.54	0.1047
Crude Oil + 0.4% EVA	4.23	0.1252	4.09	0.1210	3.98	0.1178	3.70	0.1095	3.56	0.1053
Crude Oil + 1% EVA	4.69	0.1388	4.35	0.1287	4.05	0.1198	3.85	0.1139	3.69	0.1092

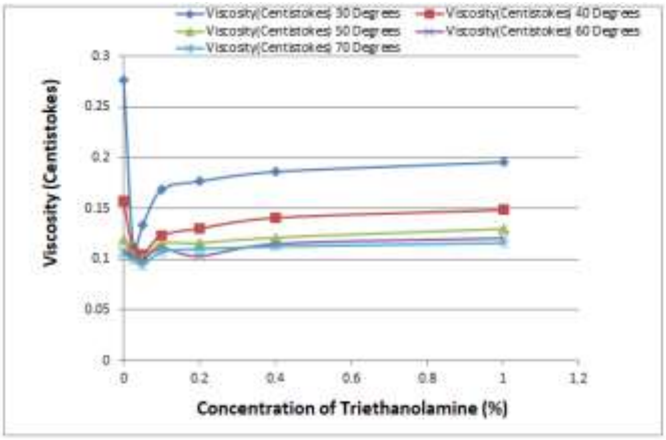

Fig.1: Graph of Viscosity against Concentration (TEA) at Different Temperatures.

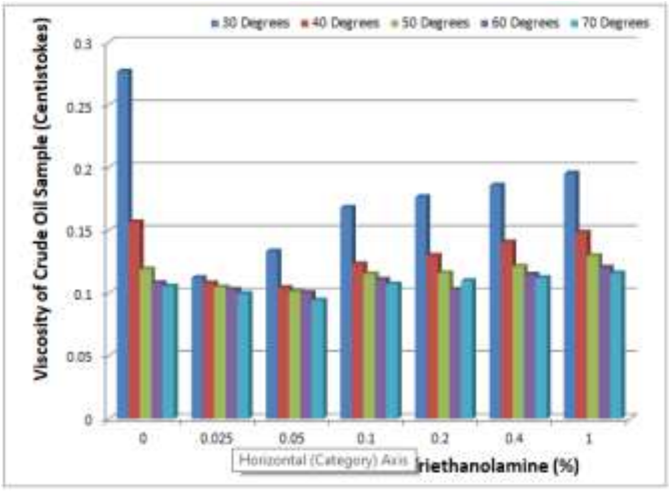

Fig. 2 Chart for Viscosity versus Concentration (TEA) at Varying Temperatures.

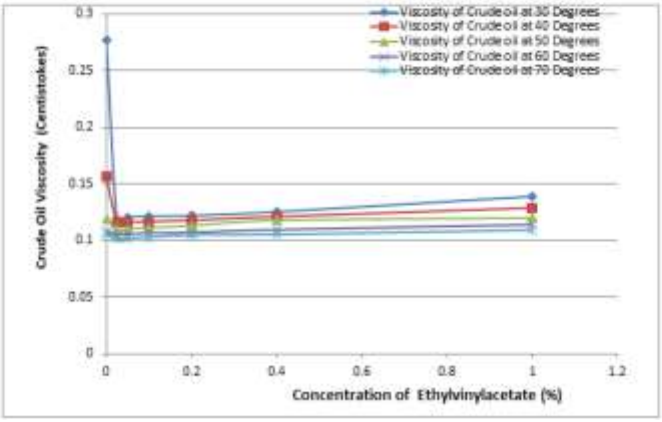

Fig. 3: Graph of Viscosity against Concentration (EVA) at Different Temperatures.

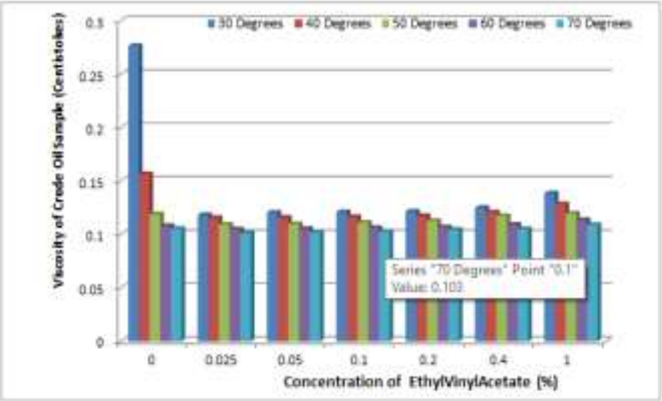

Fig. 4: - Chart of Viscosity against Concentration (EVA) at Different Temperatures

Table 3: Table of Values for the Graph of Viscosities against Concentrations of Triethanolamine at Varying Temperatures

Concentration of Triethanolamine (%)	Viscosity (centistokes) at 30°C	Viscosity (centistokes) at 40°C	Viscosity (centistokes) at 50°C	Viscosity (centistokes) at 60°C	Viscosity (centistokes) at 70°C
0	0.2767	0.1568	0.1192	0.1083	0.1056
0.025	0.1124	0.108	0.105	0.103	0.0997
0.05	0.1335	0.1045	0.1015	0.1003	0.0944
0.1	0.1684	0.1234	0.1154	0.111	0.1074
0.2	0.1767	0.1302	0.116	0.103	0.1101
0.4	0.1861	0.1408	0.1213	0.1151	0.1124
1	0.1956	0.1485	0.1299	0.1207	0.116

Table 4: Table of Values for the Graph of Viscosities against Concentrations of Ethylvinylacetate at Varying Temperatures

Concentration of Ethylvinylacetate (%)	Viscosity (centistokes) at 30°C	Viscosity (centistokes) at 40°C	Viscosity (centistokes) at 50°C	Viscosity (centistokes) at 60°C	Viscosity (centistokes) at 70°C
0	0.2767	0.1568	0.1192	0.1083	0.1056
0.025	0.1184	0.1157	0.1095	0.105	0.1015
0.05	0.1207	0.116	0.11	0.1056	0.1021
0.1	0.1213	0.1166	0.1113	0.1065	0.103
0.2	0.1219	0.1178	0.113	0.1071	0.1047
0.4	0.1252	0.121	0.1178	0.1095	0.1053
1	0.1388	0.1287	0.1198	0.1139	0.1092

2. Discussion

Effect of Temperature alone on the Crude Oil Viscosity

In all the conditions, the experiments showed a general overriding decrease in viscosity as the temperature was increased (viscosity drops with temperature rise). This applies to the raw crude oil alone, crude oil with TEA (at all percentage concentrations of TEA) and crude oil with EVA (at all percentage concentrations of EVA). Hence as temperature of the preserved crude oil sample alone was progressively increased from room temperature of 30oC to 40oC, 50oC, 60oC, and 70oC, there was consistent appreciable decrease in viscosity. This agrees with Esaklul et al., (2004) that active heating is an efficient flow assurance solution against wax.

Effects of Triethanolamine (TEA) on Crude Oil Viscosity at Different TEA Concentrations and Temperature

At room temperature of 30oC, when 0.025% of TEA by volume was introduced into the raw crude oil sample, there was a sharp reduction/decrease in viscosity from 0.2767 to 0.1124 centistokes. At subsequent higher percentages of TEA introduction to the crude oil, there was a progressive increase in viscosity but not up to the viscosity of raw crude oil, even up to 1% TEA introduction. This confirms an appreciable flow improvement/transport of the crude oil with TEA injection, keeping the optimum volume percent of injection at about 0.025% and may be below as shown in the tables 1 and 3. This agrees with the works of Soni & Bharambe,(2006), postulating that the polymeric additives at different doses are effective to depress pour point and improve flow of the crude oil up to 9oC with 500 ppm of doses.

Similar results were also obtained at higher temperatures, except that there was a further reduction in viscosity by one step or two as the temperature increases pegging the optimum concentration of the flow improver (TEA) this time at 0.05% by volume. Many temperatures were sampled and several percentage concentrations of improver injections were tested for, to serve as a check and confirmatory influence and similar trend or results were observed in each case. Furthermore, the initial drop in viscosity of the crude oil is more at room temperature (30oC) (where efficiency of the DRAs are manifested before the interference of temperatures) than at other higher temperatures.

From the graph of viscosity against concentration using TEA as flow improver (figure 1), the following observations and inferences/interpretations were obtained. The crude sample reveals initial sharp drop (by wide range) in viscosity for all temperatures (especially with lower temperatures) before rising with increased concentration of TEA for the same temperature. This indicates that TEA considerably qualifies or does the job of a flow improver with the overriding effect of temperature since room temperature was also used in the experiment as control in this case, affirming the observations of Popoola et al., (2015) and Taiwo et al., (2012), who were unanimous that TEA is a very good flow improver. Again, the lower temperatures (30oC and 40oC) recorded sharper or higher viscosity drop, implying that in the absence of the overriding effect of temperature, TEA performs very well in improving flow properties of crude oil.

Furthermore, after the initial long range sharp drop in viscosity for all cases to a minimum point, there is also a quick rise in viscosity on continued addition of TEA to each of the samples. This implies that there is an optimum point of concentration of the chemical in its results after which further concentration of TEA begins to increase viscosity instead of dropping it in concordance with Soni et al., (2005), who asserts that crude oil responds differently with the same additive at different doses, as a result of changes in rheological properties of the crude oil.

Figure 1& 2 shows that this optimum point of flow improvement result vis-a-viz viscosity is different for each sample of different temperature (though within a close range). This observation is purely an influence of higher temperature on both viscosities of crude oil and the DRA (TEA), since each line has the same composition at each point with only temperature varied.

Rate of return of the viscosity slows down drastically after quick rise and gradually tends towards a constant viscosity on further addition of the TEA. This follows the opinion of Jafari Behbahani, (2014), that relation between pour point decrease and polymeric flow improver concentration is not linear. Hence, without appropriate calculation and realisation of the minimum point, there is an imminent material or resources waste (chemical, labour, time, etc.) as further addition works in the negative of the targeted result and then tends to a useless effort. All conditions of temperature followed the same trend.

More so, the orientation of the graph of figure 1 reveals that at higher temperature (from 60oC upwards), there is a convergence or closeness of behaviour in the samples i.e. the higher the temperature, the more similar the behaviour of the flow improving process. This is suggestive that there might be convergence or optimum temperature point at which further increase in temperature will have no effect. At 60oC (which is double of the room temperature used that widely behaved differently), there is a more pronounced second irregular behaviour more than others including 70oC. The second drop or slowing down of increasing viscosity, which is not very noticeable in others was more significant around 0.1% to 0.35% concentration of TEA from where it later went higher than 70oC line as ordinarily expected from the overriding effect of temperature (confer figure 1). But then, this second optimum point for 60oC is of little or no significance for three reasons: it is happening at a higher concentration of drag reducing agent than the first optimum point which translates to material waste, happening at a higher temperature which means waste of energy, and, above all, the initial optimum point gives a better improvement/flow in the viscosity.

From the variation observed with the sample at room temperature serving as control against other higher temperature samples, it is clear that a combination of the DRA (TEA) and increased temperature gives better result as seen from the highest and lowest values of viscosity achieved across the temperatures viz: 0.0944(at 70oC) and 0.1124(at 30oC), which aligns with the opinion of Abney et al., (2003) that a combination of two or more treatment methods gives more efficient result.

The steep/sharp rise in viscosity immediately after the minimum point/drop in viscosity (figure 1) especially in the absence of heat, indicates that once the optimum point is missed, the negative result ensuing immediately after the optimum point is far disadvantageous in terms of waste of resources, time, energy and then reversal of better flow improvement already achieved.

Higher temperatures are considerably inhibitory to this reverse negative action when compared with the rate at room temperature following the large gap between 30oC and other higher temperatures graph lines. This means higher temperature degrades TEA, and Shenoy (1976) agrees with this finding that degradation can occur on the polymers during the flow due to pressure and temperature. Note: Room temperature conditions of the experiment pegged at 30oC is invariably the outside environmental seasonal temperature in most countries especially the tropics and temperate regions for consideration in pipelines.

Effects of Ethylvinylacetate (EVA) on Crude Oil Viscosity at different Concentrations and Temperature

At room temperature when 0.025% by volume of EVA was injected into the crude, there was also a sharp drop in the viscosity of the crude even though the drop for EVA was less than that of TEA. The same trend in TEA also followed after the first sharp drop. Then at subsequent higher percentages of EVA injected, the viscosity began to rise gently unlike with TEA and continued that way but never up to the viscosity of raw crude only. Room temperature readings were suggestive that the smaller the percentage EVA injected, the lower the viscosity. Each condition of temperature also shows an initial drop in viscosity to a minimum point (viscosity) before rising again. This implies also that EVA is a good flow improver. All the conditions of temperature dropping and rising simultaneously indicates that with the chemical, there is also an optimum concentration point for best result irrespective of the influence of temperature as temperature alone is expected to continuously drop viscosity or at least remain constant with further increase in temperature.

Though unarguably, temperature has an overriding effect here also, it is evident that the EVA showed its power to reduce viscosity or improve flow at the condition of room temperature pegged at 30oC. More so, the effect of temperature seems not to be much felt as the graph line of 30oC (room temperature) dropped viscosity with chemical (EVA/improver) alone closely as much as higher temperatures could offer. All temperature conditions with EVA as improver followed the same trend, although they maintained different optimum points. In any case, they are of very close range or approximately the same optimum point. Hence, high temperature does not degrade EVA as seen with TEA. Higher temperature is not inhibitory with EVA as there was no much gap between the lines. Figures 3 & 4 also show different optimum points for each temperature indicating influence of temperature alone since same composition applies in each graph line as was the case with TEA.

EVA also showed a tendency to constant viscosity by the line orientation with a seeming higher gradient towards higher concentration but didn’t have an initial steep rise as with TEA. If this happens (constant viscosity on increased concentration), it means either the DRA (EVA) is useless at higher concentration due to perfect blending with bulk crude components or it becomes inhibitory to its own action at higher concentration (because the quantities are still in parts per million).

Missing the optimum point in the case of EVA is not as disadvantageous in terms of wastes as with TEA due to the gentle initial gradient of the graph lines.

EVA did not appear to be affected by higher temperature/heat as with TEA, hence the graph line of room temperature (30oC) and other temperature are similarly close to each other except for the overriding effect of temperature. Combination of EVA with higher temperature also gave better results in terms of flow improvement as from the highest and lowest values of viscosity achieved across the temperatures, viz: 0.1015(at 70oC) and 0.1184 (at 30oC). Convergence of the different temperature lines with EVA started from the beginning and began to disperse at higher concentrations. This means higher concentration of EVA promotes reverse improver action irrespective of temperature.

Evaluation of Temperature influence over TEA and EVA as Flow Improvers

Differences

- TEA seem to have a converging optimum point at about 0.1centistokes and 0.025 – 0.05% concentration while EVA does not really seem so, rather, just showing independent drop in viscosity at different minimum points for all temperature conditions.
- There is wider range or gap in the mode of rising viscosity after the optimum point with TEA for different

temperatures even for the same concentration, whereas EVA followed a close range in-between different temperatures at the same conditions and concentration after optimum point.

- Using room temperatures for the two additives (TEA and EVA) as reference points at 0.025% concentration of each to the same volume, TEA (though more viscous than the crude oil) proved to be a better flow improver at their optimum points having 0.105centistokes against EVA having 0.1157 centistokes. The same was also observed at the apex temperature of 70oC (TEA at 0.025% concentration = 0.0997, and EVA = 0.1015centistokes at 0.025%).
- Heat degrades TEA but not EVA hence inhibits reverse viscosity.
- Increasing concentration of EVA promotes reverse viscosity drop and not heat like in TEA, hence temperature does not degrade EVA.
- TEA separates with high distinction into low and high temperatures but EVA behaved fairly uniform irrespective of the temperature.
- Second kink/depression in TEA is totally absent in EVA.

Similarities

- The two DRAs reversing viscosity at higher concentration points to the fact that either they gather the wax back with or without themselves (especially TEA) or they become immiscible compounds with wax thereby allowing the wax to nucleate back.
- Both cases (DRA/chemicals) after the fall and rise in viscosity seem to tend towards maintaining a constant viscosity (averagely) at higher concentration of the additives (about 1%) given the limits of this experiment or a kind of asymptotic behavior.
- Both DRAs compete favourably close with temperature, though it maintains an overriding effect.
- 4. The two DRAs overruled the influence of further heat and evoked a reverse viscosity trend as temperature alone would have continued reducing viscosity or remain constant at most.
- They both have optimum concentration points, beyond which wastes sets in in terms of material, energy, time, etc.
- Temperature has an overriding effect in both cases of the DRAs.
- Both varied in minimum/optimum points at different temperatures and are still closely related.
- Both also behaved in similar manner under the influence of temperature.
- Combination use of each of the DRAs with higher temperature/heat proves a better result.

IV. CONCLUSION

The influence of temperature has been placed side by side with that of triethanolamine and ethylvinylacetate with respect to flow improvement of crude oil and enhancing flow. It was discovered that although temperature has overriding influence over the actions of the two flow improvers, they competed closely almost as much as high temperatures could offer. This means, either of the DRAs can be used as an alternative to heating in flow improvement of crude oil. From the results of the experiment, it is instructive that combined use both improver and temperature gave a better result. Contrary to what one would expect, temperature did not appreciably stop the action of the improvers especially in the case of EVA. Furthermore, it was also clear that heat degrade TEA while increased concentration influences the behavior of EVA.

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