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Synthesis of ester base fluids for drilling mud formulation using different catalysts

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Abstract : The catalytic properties of potassium hydrogen sulphate, molecular iodine and sulphamic acid towards the synthesis of esters of propanol and isopropanol with lauric acid were carried out at 100and 120 ^{O}C. The most efficient catalyst at both temperatures was found to be sulphamic acid, closely followed by molecular iodine and then potassium hydrogen sulphate. Benchmarking of the products with commercially available synthetic base fluid indicated that the esters have suitable physicochemical properties for synthetic base fluid application. The results obtained from comparing the rheology of muds prepared with ester products and that with the commercially available synthetic base fluid indicate that the muds prepared with propyl and isopropyl laurate have higher electrical stability than the mud prepared with the reference base fluid. The results obtained also showed that the mud prepared with the esters synthesised in this work displayed comparable properties and performance with the mud prepared with the reference synthetic base fluid. However, isopropyl laurate (IL) formulated mud had better temperature stability than propyl laurate (PL).
Keywords : catalysts, drilling mud, ester, rheology, synthetic base fluid.

Introduction

The global trend towards increased environmental awareness and complexity of drilling operations, have led to more stringent legislations in connection with base fluids used in the formulation of drilling muds for oil and gas wells [1,2]. The first mud of choice for normal drilling operations is usually water based [3]. However, the inability of water based muds to meet the required technical performance while drilling in shale sensitive formations with potentials for pipe sticking, in addition to their thermal degradation in high temperature high pressure (HTHP) environments have necessitated their replacement with oil based muds. These oil based muds formulated with petroleum products like diesel as their continuous medium are fraught with lots of environmental pollution issues, despite their better technical performance in problematic water sensitive and clay rich geological formations [4]. The drill cuttings from such muds usually contain some percentage of residual aromatic hydrocarbons [5,6], which because of their low susceptibility to biodegradation

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accumulate in the environment after discharge of the spent muds in onshore or offshore environment. Synthetic based muds are tailored to mirror the superior technical performance of oil based muds while eliminating the environmental hazards associated with the later. Furthermore, synthetic base fluids from which these muds are formulated contain zero percent aromatic hydrocarbons [7], they can be discharged into the environment without any deleterious effect [8]. This is in addition to the fact that their reduced irritant properties lead to improved workers' safety [9]. Esters as one class of organic compounds that have served as source of base fluids for drilling mud have proved to possess good lubricating properties, low toxicity levels, as well as the capacity to be degraded both aerobically and anaerobically [3].

Esters are produced by esterification reaction between carboxylic acids and alcohols in the presence of a catalyst. Conventional homogeneous acid catalysts like H_2SO_4, HCl, HF etc. are usually employed in these reactions. However, corrosion of reaction vessels by catalyst solutions, coupled with difficult and expensive separation processes which generate large volume of waste streams are common challenges associated with homogenous catalysis [10, 11]. Solid heterogeneous catalysts and Lewis acids have emerged as green alternatives to overcome these problems, because they are noncorrosive, non-toxic and are easily separated for recycle and reuse [12, 13, 14].

Previous works on the catalytic properties of $H_3NSO_3$and $KHSO_4$ have proved that they are cheap, easily available, environmentally friendly, non-corrosive, thermally stable and moderately acidic [15, 16, 17]. Aside their capacity to catalyzethe formation of esters [18], sulphamic acid has been reported to catalyze other organic transformations like formation of ketals [19], quinoline [20], and piperidines [15], while $KHSO_4$ catalyzes the protection of carbonyls to acetals and ketals, de-protection of functional groups and the Pechmann reaction among others [21].

Molecular iodine on the other hand, has received a lot of attention as a low cost, easily available catalyst for different organic transformations like etherification [22], synthesis of dihydropyrimidines [23], acetylation of cellulose and dextran [24, 25], and synthesis of sulphones [25]. One attractive feature of iodine catalyzed esterification is its water and air tolerant properties, which allow reaction to occur in the presence of air without the need to exclude water from the reaction system with the yield of products not compromised [27].

In this work, the catalytic properties of two heterogeneous catalysts ($KHSO_4$ and H_3NSO_3), and a Lewis acid catalyst (I_2), in the synthesis of propyl and isopropyl laurate are investigated. This is primarily to determine the most effective catalyst under the experimental conditions employed for the synthesis. The physicochemical properties of the esters so prepared are benchmarked with that of commercially available synthetic base fluid. Comparison of the rheology of drilling muds formulated with the esters and mud formulated with the reference fluid at different temperatures was also carried out with the aim of determining the potential of these ester base fluids in the formulation of synthetic based drilling muds.

Materials and methods

Materials

1-propanol and 2-propanol were obtained from Xilong Chemicals; sodium thiosulphate pentahydrate were purchased from JDH Chemicals, all other reagents were purchased from Sigma-AdrichChemieGmbh. All the reagents were of analar grade and used as received without further purification. Shell Nigeria Exploration and Production Company (SNEPCo) supplied the reference fluid. All yields refer to the crude product before purification. The IR spectra were recorded in KBr discs on a system prestige 21 (Shimadzu) and recorded in the region of 4000 – 400 cm^{-1}. The IR spectral data obtained were compared with those reported in the literature. The progress of the reaction was monitored by acid value titration using 1.0 N KOH solution.

Methods

Preparation and purification of the esters

The synthesis was carried out in a reactor consisting of 250 mL three neck round bottom flask in an oil bath, heated on a thermostated magnetic stirrer. The flask was equipped with a condenser, a thermometer and a sampling port. Lauric acid (1 mol) and alcohol (3mol) were charged into the reactor and heated under reflux

till the appropriate temperature was attained. Thereafter, the catalyst (5 % w/w of acid) was added, stirring commenced and the heating under reflux continued till the end of the reaction. The weight percent of the catalyst with respect to the weight of acid and the mole ratio of the acid to alcohol were held constant at 5 % w/w and 1:3, respectively, while working at two different temperatures (100 or 120 ^{O}C). The progress of the reaction was monitored by withdrawing aliquots of the reaction mixture at intervals and analysing for acid value using 1.0 N alcoholic NaOH solution. On completion of the reaction, the reaction mixture was cooled to room temperature. In the case of sulfamic acid and $KHSO_4$ catalysed reaction, petroleum ether was added after which the mixture was filtered. Thereafter, the filtrate was washed with distilled water (100 mL × 3) in a separatory funnel to remove residual acid catalyst and subsequently dried over anhydrous sodium sulphate. The ester was recovered by subjecting it to vacuum distillation to remove both the solvent and unreacted alcohol.

The iodine catalysed reaction mixture underwent a slightly different work up procedure after the synthesis. In this case, the cooled reaction mixture was washed with concentrated sodium thiosulphate solution to remove the brown colour of iodine before extracting with petroleum ether, washing with distilled water (100 mL× 3). and drying with anhydrous sodium sulphate.The crude ester was recovered by distillation.

Determination of product characteristics

The physical properties of the two esters together with the reference base fluid were analyzed to determine the suitability of the synthesized esters as synthetic base fluids. The kinematic viscosities of the esters at 40^{O}C were determined using ASTM D 445 analytical method. The pour point and cloud point were determined using the ASTM D 97 method, while a semi-automatic Cleveland open cup flash point tester was used to obtain the flash point according to ASTM D 92 Method. Other properties of interest include density at 30 ^{o}C and specific gravity at 16.5 ^{o}C.

Mud formulation

Three different mud samples were formulated using the same quantity of base fluid and additives, following the same procedure and sequence of mixing. The mud formulated using isopropyl laurate and propyl laurate were designated as IL and PL respectively. The one formulated using the reference synthetic base fluid was designated as reference mud (RM). The procedure of the American Petroleum Institute (API) recommended practice 13B (2014) was followed in formulating the mud.

The components and quantity of the additives utilized in formulating the muds are: base fluid (210 mL), organophilic clay (20.00 g), primary emulsifier (12.00g), secondary emulsifier (7.00 mL), lime (7.00 g), brine (15.00 mL), gypsonite (3.00 g), and barite (76.00 g) as weighting agent.

Rheological properties of muds

The viscosity of the three muds at different viscometer revolutions (from 3 to 600 rpm) were determined using chandler engineering laboratory model (API) viscometer chan 35 Model (3500). The plastic viscosity (PV) and yield point (YP) were calculated from the dial readings recorded for each of the revolutions using Equations (1) and (2).

$$\mathrm{PV(cP)} = 600\mathrm{rpm\ reading} - 300\mathrm{rpm\ reading} \quad (1)$$

$$\mathrm{YP\ (lb/100\ ft^2)} = 300\mathrm{rpm reading} - \mathrm{PV} \quad (2)$$

Thereafter, each of the three mud samples were stirred at 600 rpm and left undisturbed for 10 sec before taking the 10 secgel strength at 3 rpm. The samples were also re-stirred at 600 rpm and left to stand for 10 min to take the 10 min gel strength at 3 rpm.

The electrical stabilities (ESs) of all the mud formulations were determinedin accordance with the standard test recommended by API RP 13B-2 (2014).

Effect of temperature on the mud properties

The effect of temperature on the rheology of mud prepared with propyl and isopropyl laurate was investigated at 20 ^{o}F increment from 100 to 200 ^{o}F. The mud from the reference fluid was also subjected to the same treatment. The aim was to simulate the increase in temperature as the down hole depth increases, during drilling operations.

Results and discussion

Comparison of the effectiveness of different catalysts in the esterification of lauric acid with propanol and isopropanol

A number of experiments with defined reaction parameters were carried out to investigate the catalytic activity of H_3NSO_3, $KHSO_4$ and I_2catalysts in the esterification reaction of lauric acid with 1-propanol and isopropanol. These catalysts were chosen because of their moderately strong acidic properties and their efficiency in catalyzing esterification of fatty acids. Sulphamic acid and $KHSO_4$ have the added advantage of being heterogeneous, thereby simplifying the separation process at the end of the reaction. They could also be recycled, though that aspect of their activity was not explored in this work.

The results obtained from this work indicated that H_3NSO_3has superior catalytic properties to $KHSO_4$ and molecular iodine, though the percentage conversion was reduced for the branched isomer in all cases. It also performed better at lower temperature of 100 ^{o}C and shorter duration relative to iodine which exhibited an increase in yield when the temperature was increased to 120 ^{o}C. $KHSO_4$ on the other hand displayed the lowest catalytic property under the experimental conditions investigated. The highest yield of 86 % n-propyl laurate for $KHSO_4$ catalyzed reaction was obtained at the elevated temperature of 120 ^{o}C and duration of three hours against H_3NSO_3catalyzed reaction that gave a yield of 93% of the same ester at 100 ^{o}C after 1 hour (Table 1).

Table 1: Effect of catalyst type, temperature and reaction time on the percentage conversion of the esters.

S/No	Catalyst	Temp. (^{O}C)	Time (hr)	% Conversion	
				Propyl laurate	Isopropyl laurate
1	$KHSO_4$	100	3	32	45
2	$KHSO_4$	120	3	86	42
3	Iodine	100	3	85	68
4	Iodine	120	2	92	75
5	Iodine	120	3	92	79
6	Sulphamic	100	2	95	78
7	Sulphamic	100	3	95	81
8	Sulphamic	120	1	93	39
9	Sulphamic	120	3	93	72

Reaction conditions – 1: 3 mole ratio (acid:alcohol), 5% catalyst (wt of catalyst/weight of acid)

Equations (3) and (4) were employed for calculating the acid value and percentage conversion of the acids to esters, respectively.

$$AV = \frac{\mathrm{Vol}_{NaOH} \times C \times 40}{1g\ \text{of sample}} \quad (3)$$

$$\% \text{ Conversion of acid} = \frac{AV_1 - AV_2}{AV_1} \times 100 \quad (4)$$

AV = Acid value.

Vol_{NaOH}= volume of NaOH required to reach endpoint

C= Molar concentration of NaOH.

40g/mol = Molar mass of NaOH.

AV_1 = acid value of lauric acid in mg/mLNaOH.

AV_2 = acid value of the ester at the end of the reaction.

Benchmarking of the esters through their physicochemical properties

The laurate esters were produced to 1 litre volume by the sulphamic acid catalyzed synthesis on the basis of its superior catalytic properties. The fundamental physicochemical properties of the base fluids like density, viscosity at 40 ^{o}C, flash point and pour point were determined and compared with the corresponding properties of the reference. The results (Table 2) show that the esters have comparable physicochemical properties with the reference. However, isopropyl and propyl laurate have higher flash and fire points than the reference, while propyl laurate has the highest flash and fire points of the three. Thus the trend for the flash point and fire point is in the order: propyl laurate>isopropyl laurate> reference fluid. It seems therefore that the introduction of branching in the isopropyl isomer led to a decrease in the flash point of the ester. Apart from the greater potential for fire hazard implied by the lower flash point of the reference base fluid compared to IL and PL, an insight into the storage and transport requirements of the base fluid can also be obtained from the flash point determination [28].

Table 2: Properties of the esters produced in this study and the reference base fluid.

Properties	**PL**	**IL**	**Reference base fluid**
Density at 30 ^{o}C	0.852	0.842	0.808
SG at 16.5 ^{o}C.	0.856	0.846	0.813
Viscosity at 40 ^{o}C (cSt)	4.160	4.160	3.000
Flash point (^{o}C)	127.8	121.7	103.9
Fire point (^{o}C)	146.1	142.9	126.7
Cloud point (^{o}C)	8	13	17
Pour point (^{o}C)	-7	-6	<-4

The result also showed that the cold temperature properties of the two synthesized esters are marginally better than that of the reference as reflected by their lower pour point relative to the reference.

The kinematic viscosity of propyl laurate and isopropyl laurate have higher values than that of the reference fluid, however, the adverse effect on the rheology of the mud can be reduced by appropriate design of the drilling fluid formulation.

The $H_3NSO_3$and $KHSO_4$ synthesized esters were clear colourless liquids, while the products obtained from iodine catalyzed reactions were light yellow in colour after work up and vacuum distillation.

Thus, the physichochemical properties of the propyl laurate and isopropyl laurate esters are comparable to the reference fluid and, therefore could be utilized as base fluids in the formulation of synthetic base muds.

Rheological properties

The results of the mud rheology tests

The result of the ES test revealed that the ES values of both IL and PL formulated muds are higher than that of the reference mud. The higher electrical stability of IL and PL based muds relative to the reference indicates that they have better water-oil emulsion stability and oil-wetting capability than the reference mud sample. The results obtained for all the mud formulations are presented in Table 3.

Table 3: Electrical Stabilities and Rheological properties of the muds at 100 ^{o}F

Property	**IL**	**PL**	**RM**
PV (cP)	18	10	15
YP(lb/100ft^2)	12	5	7
10sec (lb/100ft^2)	7	3	3
10min (lb/100ft^2)	11	5	3
Electrical stability (volts)	985	1052	978

The results obtained from the mud rheology determination (Table 3) showed that the PV, YP, 10 sec gel strength and 10 min gel strength of IL are all higher than the values recorded for the reference mud, these values however, were lower for the PL mud except for the10 sec gel strength that are the same. The lower PV value (10 cP) of the PL mud indicates that it would offer lower resistance to flow relative to the IL and RM muds with PV of 18 and 15 cP, respectively. This will lead to reduced circulating pressures capable of bringing about good hole cleaning and preventing loss of circulation, thereby reducing pumping costs. These values for the three muds however, are still within the recommended values required for drilling muds [29]. The higher YP of the IL mud (12 lb/100ft^2) is indicative of a potentially better carrying capacity of the IL mud relative to both the PL and RM muds with yield points of 5 and 7 lb/100ft^2, respectively. However, the 10 sec and 10 min gel strength of the reference mud recorded the same value of 3 lb/100ft^2, while the PL mud registered slight increase from 3 to 5 lb/100ft^2. The lower gel strength of the PL and RM muds is indicative of the fact that the muds will remain pumpable with time after drilling is interrupted. It was observed that the IL mud apart from having higher gel strengths, also recorded the highest increase in value from 7 to 11 lb/100ft^2. Thus, while the PL mud and RM exhibit flat gel structure, the IL mud exhibits progressive gel structure. A flat gel structure is usually preferable to a progressive gel structure that increases over time in drilling operations because it allows for lower pump pressure to commence drilling after interruption of the drilling process.

The viscometer readings (in revolution per min) of the three muds were converted to shear rates and plotted against the shear stress to obtain similar rheograms which fit into the Bingham model (Figure 1), indicating that the flow behaviour of the IL and PL muds are similar to that of the reference. Generally, it was observed that the IL mud recorded the highest shear stress at the same shear rate and temperature.

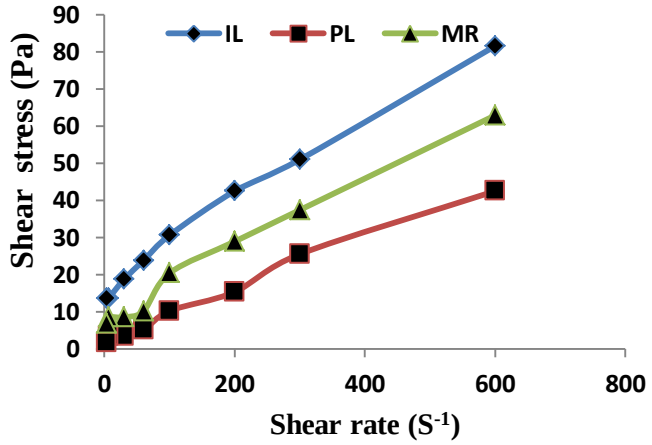

Fig.1: Rheogram of IL, PL and RM muds at 100^{o}F

The effect of temperature on the mud properties

The effect on mud properties as the downhole temperature increases was modelled by investigating the effect of temperature on the rheology of muds between 100 and 200 ^{o}F and the results presented in Figures 2 through 5. These results indicated that the mud formulated with IL continuously maintained higher plastic viscosity values than the reference mud and PL mud all through the temperature range investigated. On the other hand, the reference mud recorded higher PV values than the PL mud at all the temperatures except at 160and 180 ^{o}F where they both recorded the same value of 11 cP.

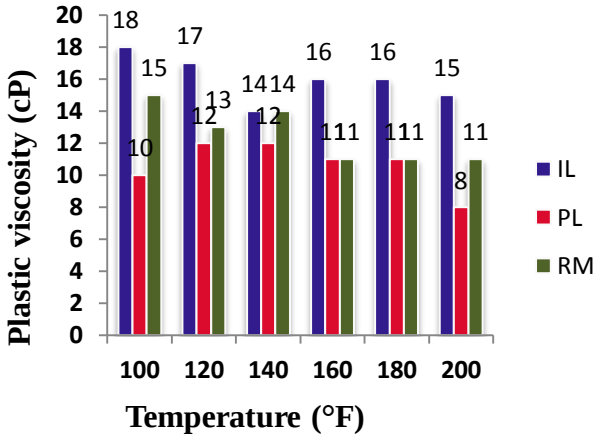

Fig.2: Effect of temperature on the plastic viscosity of the muds

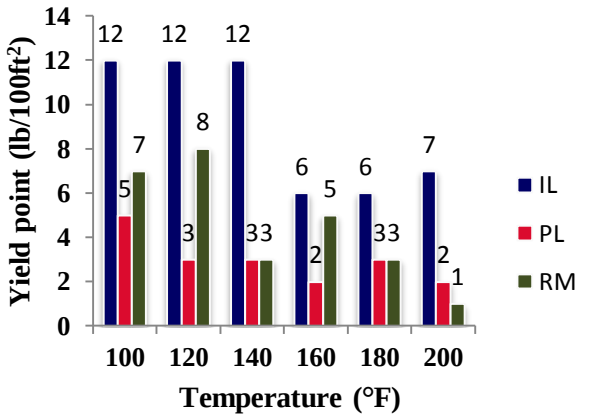

Fig.3: Effect of temperature on the yield point of the muds

The IL mud also displayed higher yield point values at all the temperatures investigated, followed by the reference and the PL mud in that order. This is understandable, since IL recorded higher viscometer readings relative to the other muds. Though high PV value is not a desirable mud property, high YP within the recommended values is a required property, because mud with high YP will exhibit better carrying capacity for the drill cuttings during drilling operations relative to another mud with the same density. Thus, in terms of YP, the PL mud with the lowest YP values will perform better than the IL mud and the reference mud (Fig. 3).

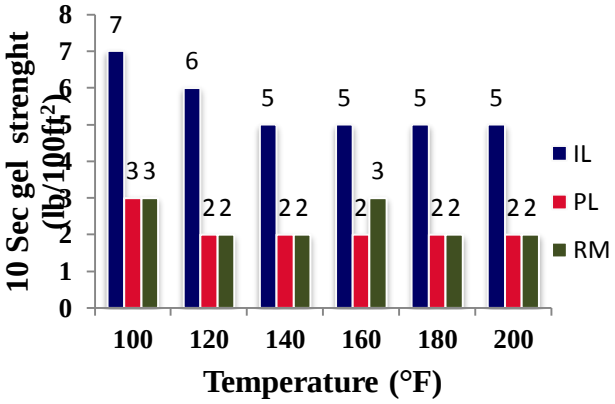

Fig.4: Effect of temperature on the 10 sec gel strength of the muds

The 10 mingel strength of the IL mud ranged from 7 lb/100ft^2 at 100 ^{o}F to 6 lb/100ft^2 at 120 ^{o}F. Thereafter, it maintained a constant value of 5 lb/100ft^2 from 140 ^{o}F through 200 ^{o}F. The same trend was noticed for the reference mud and the PL with the 10 min gel strength of 3 lb/100ft^2 at 100 ^{o}F and a constant value of 2 lb/100ft^2 throughout the temperature range investigated. The PL mud however, recorded a value of 3 lb/100ft^2 at 160^{o}F. Thus the IL mud displayed the highest 10 min gel strength values of all the muds at all temperatures (Fig. 4).

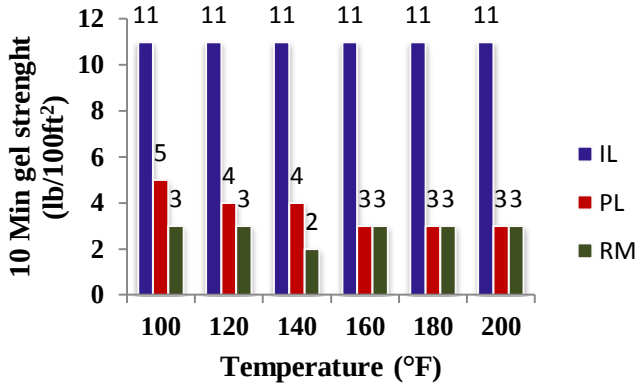

Fig.5: Effect of temperature on the 10 min gel strength of the muds

The gel strength for the IL mud at 10 min was constant (11lb/100ft^2) from 100 through 200°F. The reference mud also maintained a value of 3lb/100ft^2 at all the temperatures except 140 °F, where the value came down to 2 lb/100ft^2**.** Thusthe difference between the gel strength of the reference mud at 10 sec and 10 min is 1 lb/100ft^2. The PL mud recorded values of 5 lb/100ft^2 at 100 °F and 4 lb/100ft^2 at 120 and 140 °F. Thereafter, gel strength remained constant at 3 lb/100ft^2.

Conclusion

From the results obtained in this research, we can conclude as follows;

1. Sulphamic acid displayed the best catalytic activity towards the synthesis of propyl laurate and isopropyl laurate.
2. Propyl and isopropyl laurate have comparable physicochemical properties relative to the reference, but have higher flash point and better cold temperature behaviour than the reference fluid.
3. Propyl and isopropyl laurate muds exhibited better emulsion stability than the reference mud.
4. Isopropyl laurate consistently displayed a high potential for utilization as a synthetic base fluid for drilling mud formulation, while propyl laurate displayed comparable properties albeit with lower viscosity values relative to the reference.

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