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A Controlled Experiment to Determine the Effect of High Formation Water Salinity on Crude Oil in Hydrocarbon Bearing Rock

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Abstract: ***Having knowledge of formation water salinity can have dramatic consequences in the evaluation and assessment of a hydrocarbon bearing reservoir, produce water salinity analysis therefore plays a role in dynamic modelling of reservoirs, quantifying reserves and calculating completion cost, including how much will be spent on casing and surface equipment-capital expenditures (capex). Water analysis also helps operators estimate operating expenditures (opex), such as the cost of chemical injection.. This research work examined the effect of high formation water salinity on the physicochemical and thermophysical properties of crude oil system by injecting different concentration of synthetic brine solutions (25%, 50%and 75% Brine solutions) in to the crude oil at different operating conditions and parameters like PH, Viscosity (Cst), Specific Gravity, API / Baume, TDS (mg/l), EC (µScm-1), Colour (PtCo), Density (lb/Gal.) were determined. Test result indicated that formation water with highest salinity showed highest incremental values in the measured physicochemical and thermophysical properties at different operating conditions. This research analysis therefore, helps development planner determine whether new discoveries can be tied into existing infrastructure and is also crucial for designing water injection project.***

Keyword: Baume, TDS, Brine solution, Physicochemical properties, Thermophysical properties

1. Introduction

Many of today's oil reservoirs are composed of sediments, which were once deposited in Marine, deltaic and other aquatic environments. Consequently, these sedimentary beds were originally saturated by salt water. Part of this water was displaced in the process of diagenesis and oil accumulations, the other remains, suspending the hydrocarbons because of their density contrast. That which remains generally is known as "Connate" or "Interstitial" water because the water was "born with" and is stored in the interstices of the sediments. Thus, reservoir rocks normally contain both petroleum hydrocarbons (liquid and gas) and water. Sources of this water may include flow from above or below the hydrocarbon zone, flow from within the hydrocarbon zone, or flow from injected fluids and additives resulting from production activities. This water is also referred to as connate water or formation water and becomes produced water when the reservoir is produced and these fluids are brought to the surface [1].

The composition of this produced fluid is dependent on whether crude oil or natural gas is being produced and generally includes a mixture of either liquid or gaseous hydrocarbons, produced water, dissolved or suspended solids, produced solids such as sand or silt, and injected fluids and additives that may have been placed in the formation as a result of exploration and production activities [6].

Produced water is not a single commodity. The physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geological formation with which the produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced. Produced water properties and volume can even vary throughout the lifetime of a reservoir. If water-flooding operations are conducted, these properties and volumes may vary even more dramatically as additional water is injected into the formation.

Waters from petroleum formations generally contain many ions. Sodium and chloride ions are usually present in high concentrations, while other ions are present in wide ranging quantities. Knowledge of the constituents of specific produced waters is needed for regulatory compliance and for selecting management/disposal options such as secondary recovery and disposal. Oil and grease are the constituents of produced water that receive the most attention in both onshore and offshore operations, while salt content (expressed as salinity, conductivity, or TDS) is a primary constituent of concern in onshore operations [4].

In addition, produced water contains many organic and inorganic compounds. These vary greatly from location to location and even over time in the same well. The organic and inorganic components of produced water discharged from offshore wells can be in a variety of physical states including solution, suspension, emulsion, adsorbed particles, and particulates [2,3,5].

Salinity refers to the amount of total dissolved salts (TDS) in the water and is frequently measured by electrical conductivity (EC), because ions dissolved in water conduct electricity and actual TDS analyses are expensive to conduct. Waters with higher TDS concentrations will be relatively conductive. TDS is measured in parts per million or mg/L and EC is measured in micro-Siemens per centimeter (µS/cm).The objective of this research work therefore is to determine the effect of high formation water salinity on crude oil inside a hydrocarbon bearing rock called Petroleum reservoir.

2. Materials and Methods

Sampling:

All the collected samples were preserved in accordance with guidelines and International Standards. All other QA/QC procedures relevant to sample collection, custody and analyses were strictly adhered to. (APHA 1995; ASTM, 1979). The crude oil sample was obtained from Forcados oil field, Nigeria. Synthetic reservoir brine solutions were prepared using distilled water treated with 5%, 25%, 50%, and 75% concentrations of Sodium Chloride. A heating bath was used to raise sample temperatures as required. Experiments were replicated to enhance accuracy of Measurements. Physico-chemical and Thermophysical properties analysis that were carried on the crude oil involve; Density, specific gravity, API gravity, Potential hydrogen oil concentration, Electrical conductivity and viscosity. Due diligent were taken to prepare the samples for specified test as indicated below:

Chloride (APHA 2520A): These were determined titrimetrically. About 25ml of the sample was measured in a beaker and a drop of potassium chromate indicator added. The solution was titrated with AgNO3 solution until the appearance of brick red colour as the end point. The amount of chlorine (mg/l) was obtained as

$$CL = \frac{(F \ X \ 0.3 \ X 1000)}{V}$$

Where F = volume of $AgNO_3$ titrated and V = volume of sample

Viscosity determination: The crude sample was charged into the viscometer and placed in the water bath which was then switch on. The thermostat set at 35^0 F was inserted into the bath to regulate the temperature of the water in the bath. The temperature was set and placed inside the water bath through an opening made for it. The crude sample was adjusted to a set mark in viscometer, the stop clock is started and the time at which the crude flow from the upper mark to the lower mark was recorded and the viscosity was calculated from its flow rate as follows.

$$K_V = C_V \text{ X T}$$

Where K_V = Kinematic viscosity (cst), C_V= Viscosity constant = 0.09636 and T = flowing time (secs).

PH Value determination: A 4 parts pH measuring system was used for ph determination namely: a ph sensing electrodes, electronic circuit that translate the signal into readable reference for the user and the sample being measured. A 9 volt battery was connected to the ph meter, the cover was adjusted to desired view angle, the meter was switch on and the mode was set to ph position, this activated the liquid crystal display, the cable was connected to the BNC input and the electrode was conditioned in buffer 7.0 solution until the LCD is stable (30 sec) the temperature control was adjusted to ambient temperature, the buffer and the samples was allowed to come to this ambient temperature ,the calibration control was adjusted in such a way that the LCD showed the value of buffer 7.0 at 250oF,the electrode was then rinsed with buffer 4.0, blot dry and immersed in buffer 4.0 when the LCD is stable (30sec) the slope control was adjusted to make LCD show the value of 4.0 solution, the system has now been calibrated to read sample with different ph values. The electrode was the rinsed with a small portion prepared crude sample, blot dry and immerse in the sample. This was repeated for measuring the ph value of all the prepared crude samples.

Density determination: 50 ml pycometer (density bottle) was rinsed with distilled water and dry with acetone, the mass of empty pycometer was measured and recorded using analytical balance, the pycometer was then filled with distilled water, the stopper was inserted and the stopper hole was also filled with distilled water, it mass was measured recorded, the pycometer was then filled with distilled water and dry with acetone, the pycometer was the filled to the brim with the crude oil sample, the pycometer was then hanged in thermostat bath at the given temperature and was allowed for a few minutes to reach equilibrium, the pycometer was the removed from the bath, wipe dry and weigh on an analytical balance, the density of oil sample was obtained as

$$D = \frac{M_W}{V_M}$$

Where D = density (lb/bbl), M_W = Molecular weight (lb) and V_M= volume (bbl)

Determination of specific gravity 60^0F : The sample was prepared and transferred into a clean gravitometer cylinder, the gravitometer was then lowered gently into the sample and it was sealed, it was then depressed to about two scale division into the liquid and then it was sealed, sufficient time was then allowed for the gravitometer to become completely stationary and for air bubbles to surface, when the gravitometer finally comes to rest and floating freely, the Gravitometer was read to the nearest scale division, the correct reading is that point on the gravimeter scale at which the liquid cut the scale. The point was determined by placing the eye slowly below the level of the liquid and raising it slowly unto the surface until a disturbed eclipse appears to be a straight- line crossing the gravimeter scale. Note that for conversion of specific gravity at laboratory temperature (^{0}F) to value at 60 ^{0}F, the equations below were used

$$SG = \frac{\rho_F}{\rho_W}$$

Where SG =Specific Gravity (dimensionless), ρ_F = Density of fluid (kg/m^3) and ρ_W = Density of water (kg/m^3).

API gravity determination: The sample was prepared and transferred into a clean gravitometer cylinder, the gravitometer was then lowered gently into the sample and it was sealed, it was then depressed to about two scale division into the liquid and then it was sealed, sufficient time was then allowed for the gravitometer to become completely stationary and for air bubbles to surface, when the gravitometer finally comes to rest and floating freely, the Gravitometer was read to the nearest scale division, the correct reading is that point on the gravimeter scale at which the liquid cut the scale. All the samples for ph measurement were maintained at 60^0F, and the ph was calculated from the correlation.

$$°API = \frac{141.5}{SG \ @60°\text{F}} - 131.5$$

Electrical conductivity (EC) determination: A saturated paste of samples of crude oil was prepared. The electrical conductivity of the sample was determined electrometrically with a calibrated electrical conductivity meter.

Heavy Metals Determination (AAS): Samples were pre-treated with 2ml conc. HNO3 per litre of sample. The equipment was conditioned by auto-zeroing it with distilled water and with conc. HNO3. The pre-treated sample was analysed for heavy metals using the appropriate hollow cathode element of each metal of interest at the appropriate wavelength, lamp current, band-pass, and background correction.

Oil and Grease Determination (ASTM D 3921): About 100ml acidified sample (pH 2) was measured into a graduated glass bottle. 4ml of an organic solvent was added to the sample and the bottle vigorously shook for 2mins. The contents of the bottle were emptied into a separating funnel and shook vigorously. The stopper of the funnel was intermittently opened to release pressure build up. The contents of the funnel were allowed to settle. The bottom layer of the solution was transferred into a clean beaker using glass funnel previously stuffed with cotton wool and 1g anhydrous sodium sulphate at the aperture of the glass funnel to absorb water.

Ammonia (APHA 4500C): About 50ml of the sample was measured into distillation flask. 0.4g of magnesium oxide was added and distilled into a beaker containing 10ml of 2% boric acid and combined indicator. This was titrated back with 0.1M HCl and the titre value was recorded.

$$NH_3 \text{ (Mg/l)} = \frac{(F\ X\ 100)}{V}$$

Where F = titre value and V = sample volume used

Phosphate Determination (APHA 425C): About 1 drop of phenolphthalein indicator was added to 100 ml of the sample. 4ml of the molybdate reagent was added and mixed thoroughly. About 0.5ml stannous chloride was added, making sure that all reagents were maintained between 20-30oC. After 10 minutes, the absorbance was measured at 690nm with 10mm cell curvet.

$$PO_4^{3-} \text{ (Mg/l)} = \frac{(F\ X\ 100\ X\ D)}{V}$$

Where F= reading from curve, D = dilution factor.

Sulphate Determination (APHA 427C): About 20ml Buffer solution A was added to 100ml of the sample and the contents mixed. While stirring, a spoonful of barium chloride crystals was added and timing was started immediately. After 1min stirring at constant speed, the solution was poured into 10mm cell and measured within 5mins at 425nm.

$$SO_4^{2-} \text{ (mg/l)} = \frac{\text{F X 100}}{\text{V}}$$

Where F = reading from curve, D = dilution factor.

Physico-chemical analysis: ph/temperature (apha 460), conductivity (apha 145), and tds (apha 208d): These chemical properties were determined electrometrically with a multi- parameter data logger (Hanna model HI991300).

3. Result and Discussion

It was observed from the Test result of thermophysical and **physicochemical** properties of the crude oil system (Table 1) that, concentration of parameter like viscosity, specific gravity, density decreased with rise in temperature while parameter like EC, TDS,and Ph increased with rise in temperature.

Table 1: Analysis of the physicochemical and Thermophysical properties of crude oil system @ different operating conditions

S/N	*Properties*	*A*	*B*
1.	Temperature. (^{0}F)	77	177
2.	PH	4.54	5.12
3.	Viscosity (Cst)	3.8	1.69
4.	Specific Gravity	0.788	0.7637
5.	^{0}API / Baume	48	54
6.	TDS (mg/l)	51	78
7.	EC (µScm^{-1})	105	155
8.	Colour (PtCo)	20	10
9.	Density (lb/Gal.)	6.60	6.35

A= **100% Crude oil @ 77^0 F,** B = **100% Crude oil @ 140^{0}F,**

Table 2: Analysis of the physicochemical and Thermophysical properties of crude oil + 25% Brine solution @ different operating conditions

S/N	*Properties*	*A*	*B*	*C*	*D*
1.	Temperature. (^{0}F)	77	177	77	177
2.	PH	4.54	5.12	6.20	7.10
3.	Viscosity (Cst)	3.8	1.69	4.2	2.9
4.	Specific Gravity	0.788	0.7637	0.816	0.802
5.	^{0}API / Baume	48	54	42	45
6.	TDS (mg/l)	51	78	70	90
7.	EC (µScm^{-1})	105	155	115	150
8.	Colour (PtCo)	20	10	17	8.0
9.	Density (lb/Gal.)	6.60	6.35	6.79	6.68

C = **crude oil + 25% Brine solution @ 77^0 F,** D = **crude oil + 25% Brine solution @ 140^{0}F,**

(Table 2) indicated that, the addition of 25% brine solution increased most of the tested paramerter (both at lower and higher temperature) except Baume, Ph increased from 4.45 to 6.20 on addition of 25% brine solution, this trend was also seen at higher temperature. This can be attributed to the presence of sodium chloride in the brine solution which neutralises the acidity of the crude oil. Vicosity also increased from 3.8 to 4.2 on addition of 25% brine solution. This could be attributed to increase in the degree of interaction or bonds between crude oil molecules on addition of brine solution. Density increased from 6.60 to 6.79 on addition of brine solution.. This could be attributed to the presence of higher concentration of brine inherent added solution. TDS increased from 51 to 70 on addition of 25% brine solution, this could be attributed to a higher concentration of suspended and dissolved solid inherent in formation water samples. Specific gravity increased from 0.788 to 0.816 , this can be attributed effect density increase, the higher the density the higher Specific gravity.

Table 3: Analysis of the physicochemical and Thermophysical properties of crude oil + 50% Brine solution @ different operating conditions

S/N	*Properties*	*A*	*B*	*E*	*F*
1.	Temperature. (^{0}F)	77	177	77	140
2.	PH	4.54	5.12	9.7	8.1
3.	Viscosity (Cst)	3.8	1.69	5.0	3.2
4.	Specific Gravity	0.788	0.7637	0.993	0.973
5.	^{0}API / Baume	48	54	11	14
6.	TDS (mg/l)	51	78	105	120
7.	EC (µScm^{-1})	105	155	205	375
8.	Colour (PtCo)	20	10	15	7
9.	Density (lb/Gal.)	6.60	6.35	8.27	8.10

E = **crude oil + 50% Brine solution @ 77^0 F,** F = **crude oil + 50% Brine solution (140^{0}F)**

It was observed that addition of 50% brine solution (Table 3) follows the same trend as in table 1 but with higher values, PH, Viscosity, Specific Gravity,0API / Baume, TDS, EC Colour, Density increased from 4.54,3.8 (Cst), 0.788, 48,51(mg/l),105(µScm-1),,20(PtCo),,6.60(lb/Gal.) **to** 77,9.7, 5.0, 0.993,11, 105, 205 (µScm-1), 15(PtCo),,8.27(lb/Gal.) respectively on addition of brine solution. Table 4 also followed the same trend with table 2 and table 3 but with highest values.

Table 4: Analysis of the physicochemical and Thermophysical properties of crude oil + 25% Brine solution @ different operating conditions

S/N	**Properties**	**A**	**B**	**G**	**H**
1.	Temperature. (^{0}F)	77	177	77	140
2.	PH	4.54	5.12	10	10.9
3.	Viscosity (Cst)	3.8	1.69	7.3	6.4
4.	Specific Gravity	0.788	0.7637	1.218	1.260
5.	^{0}API / Baume	48	54	26	30
6.	TDS (mg/l)	51	78	325	450
7.	EC (µScm^{-1})	105	155	238	520
8.	Colour (PtCo)	20	10	5	0
9.	Density (lb/Gal.)	6.60	6.35	10.15	10.50

G = **crude oil + 75% Brine solution @ 77^0 F**, H = **crude oil + 75% Brine solution @ 140^{0}F,**

Comparing table 1,2,3 and 4 , it was observed that the concentration of the physicochemical and thermophysical properties of crude oil increases with increased in concentration of Brine in the added solution, 25% showed lowest value, 50% showed higher values, and 75% showed the highest value

4. Conclusion

Having knowledge of formation water salinity can have dramatic consequences in the evaluation and assessment of a hydrocarbon bearing reservoir. The specific type of salinity identification test chosen to be conducted in the laboratory on core is very much dependent on the actual mineralogy of the formation and its physical properties. An understanding to the chemistry of formation waters in sedimentary basins is also important for many geological processes, such as the fluid-rock interaction, the migrating paths of fluid and the entrapment mechanisms of hydrocarbon. This research work shows that the concentration of the physicochemical and thermophysical properties of crude oil increases with increased in concentration of Brine in the crude oil system and vice versa. Specific ions present in the brine can also influence interfacial film behavior. The effect of brine composition on interfacial film and emulsion stability should be carried out as the future scope of this research work

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