(SSZC 2022) J. Chem. Soc. Nigeria, Vol. 47, No. 4, pp 921 – 930 [2022]

FOAM STABILIZATION AND INTERACTIVE PROPERTIES OF KONO-BOUE CLAY NANOPARTICLES IN OIL RECOVERY

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ABSTRACT

Different materials have been employed in chemical enhanced oil recovery (CEOR) to recover more residual oil from reservoir rock formations. Surfactants have been used though better recovery margin is expected when in conjunction with nanoparticles (NPs) (Silica and more recently clay). This combination reduces surfactant loss to the reservoir formation and enhances foam stability. The interactive properties and foam stability of locally available Kono Boue (KB) clay NPs were studied to establish its suitability for applications in CEOR. The KB clay NPs were synthesized using Sodium Dodecyl Sulphate (SDS) mediated (sol-gel) route and characterized with X-ray Diffraction (XRD), Energy Dispersive X-ray Fluorescence (EDXRF), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FT-IR) spectroscopy, Wettability alteration, Interfacial Tension (IFT) and Foam stability. The XRD and EDXRF confirmed the clay as Kaolinite (Al > 16 %; Si > 30 %). Surface morphologies showed platy polycrystallites of different sizes on the SEM while characteristic vibrations of Si-O stretching (780 and 1056 cm^{-1}) and Al-OH bending (698 cm^{-1}) vibrations were obtained from the FT-IR. Control of particle sizes (85, 63, 66, 60, 66 and 90 nm) was achieved using different concentrations (0, 2.08, 6.25, 8.33, 10.42 and 14.58 mM) respectively of SDS at constant clay particles (10 g). The samples were calcined at 900 °C for 2 h. IFT reduction between the oil and the aqueous media at constant SDS concentration increased with decrease in particle sizes from 85 to 60 nm. Similarly, wettability alteration also showed changes from nearly neutral-wet towards more water-wet condition with particle size variation. The foam stability experiment confirmed that the clay NPs with the least particle size of 60 nm gave the most stable foam.

Keywords: Nanotechnology, Clay nanoparticles, Kono Boue clay, Foam stability, Interfacial tension

INTRODUCTION

Nanotechnology has emerged as one of the leading innovations in the oil industry as their unique properties, size and large surface area cover a whole range of applications. NPs are particles ranging from 1 to 100 nm in size and they form nanofluid which has improved properties when they are in contact with a base fluid [1-3]. Their applications cut across many disciplines such as medicine, science, oil and gas industry etc. [4]. NPs find its usefulness in CEOR as additives that improve the recovery of trapped oil in reservoirs. Oil recovery using chemical method is one of the effective ways to improve recovery by adding chemicals such as polymers, alkalis and surfactants to water.

This process is achieved by decreasing both the capillary number and oil mobility ratio [5]. Surfactants are surface active agents that are amphiphilic in nature. Surfactant solution when injected into the oil reservoir, changes the rock formation's surface activities by lowering the IFT at the reservoir rock/oil/water, thereby lowering the high capillary forces. As a result, more oil is displaced [6, 7, 8]. Surfactants can alter the wettability of a formation from oil-wet towards more water-wet formations [9]. Despite its significance in CEOR, there is loss of surfactant due to their adsorption on the rock formations. Thus, too much surfactant is used, and the high cost of chemicals made its use economically infeasible [9, 10]. Surfactants can form unstable gas bubbles known as foam when dispersed in an aqueous medium. Formability and foam stability are described as surfactant's capacity to form foam and variation of the foam height with time respectively. The interaction of foam and crude oil is a function of its stability [11-12] and the solubilization of crude oil is determined by surfactant's capacity to stabilize foam [13].

NPs exhibit better recovery margin when used with surfactant in CEOR as they tend to lower the surfactant loss due to adsorption on the rock formations [14]. Several NPs have been used in Enhanced Oil Recovery (EOR) such as silicon oxide, zinc oxide, iron oxide NPs. Most of them are expensive and not easily accessible. Hence, the need for locally available NPs arises. Clay minerals belong to the phyllosilicate group consisting of octahedral and tetrahedral sheets [15]. Clay has been used for the synthesis of clay NPs and they are readily availability and cost effectiveness makes the use economically viable. Naman and Sudhanshu [16] successfully exfoliated and extracted clay NPs from bentonite soil with a significant change in crystal lattice structure with cationic surfactant while the reverse was observed for anionic and non-ionic surfactant. Goshtasp and Seyyed studied the role of clay NPs on adsorption of surfactant on solid surfaces [17]. They discovered that 52% of heavy crude oil was recovered by addition of SDS to NPs. Agrawal et al. [18] investigated on the use of treated NPs for reducing the adsorption of surfactant in clay containing oil reservoirs and concluded that NPs significantly reduces the surfactant adsorption in reservoir [18]. First report of KB clay by Gbarakoro et al. [19] showed that KB clay is richer in silica than Alumina. Therefore, there are prospects that locally available KB clay could be used as a cheaper alternative material to SiO_2 NPs. This study will investigate the interactive properties and foam stability of KB clay NPs with crude oil, surfactant and brine for possible application in EOR.

MATERIALS AND METHODS

The Clay used in this study was collected from KB, Khana Local Government Area, Rivers state, Nigeria. SDS (99.9% pure) was purchased from British drug house, United Kingdom. Molecular formula of $C_{12}H_{24}SO_4Na$ with molecular weight of 288.38 g/mol. Crude oil is a light oil (American petroleum institute, 31.14°), density 0.8704 g/ml, viscosity 10.4832 cP and specific gravity of 0.8700 at ambient temperature of 29 °C, gotten from Obelle flow station, Port Harcourt, Rivers state. 30 g of NaCl salt was dissolved in 800 ml of distilled water and made up to l L mark. 0.60 g, 1.80 g, 2.40 g, 3.00 g and 4.20 g of SDS were weighed and dispersed in 800 ml of distilled water and made up to 1 L mark, to prepare a standard solution concentration of 2.08, 6.25, 8.33, 10.42 and 14.58 mM respectively.

Synthesis of Clay NPs

The clay material was oven dried at 120 °C for 3 h for the moisture to be completely evaporated. The dried clay was ground into fine grain particles and sieved with 100 mm mesh. The sieved clay particles (10 g) were dispersed in 300 ml of distilled water and stirred with a magnetic stirrer for 90 minutes. The distilled water was decanted and the particles were further washed thrice with distilled water to remove impurities, and then dried in an oven at 110 °C for 24 h. This was followed by calcination in a furnace at 900 °C for 2 h for the control experiment. The procedure was used each for SDS mediated KB clay NPs by dispersing 10 g of the sieved clay particles in 50 ml of various SDS concentrations 2.08, 6.25, 8.33, 10.42 and 14.58 (mM) respectively in place of distilled water..

Characterization

The clay NPs and SDS mediated clay NPs were analyzed. X-ray diffraction (XRD), Energy Dispersive X-ray Fluorescence (ED-XRF), Fourier Transform Infrared (FT-IR) spectroscopy and Scanning Electron Microscopy (SEM) were done to determine crystallinity, elemental compositions, functional groups and surface morphology of the clay NPs respectively. The mean particle sizes were estimated using Debby Scherrer's formula.

$$D = \frac{K\lambda}{d\cos\theta} \qquad (1)$$

where K = Scherrer's Constant, λ = Wavelength of the X-ray source, d= Full Width at Half Maximum in radians, θ = Peak Position in radians, D= Mean crystallite size (nm).

Interactive Properties

The IFT between the clay NPs/SDS/brine and crude oil was determined by first measuring the individual surface tension. The surface tension in air of clay NPs dispersed in distilled water and at constant SDS concentration (8.33mN/m) was determined with survismeter to measure the liquid drop behavior in the capillaries. The numbers of drops made by the liquid within the capillaries tube's upper and lower mark are determined for surface tension measurement [20]. The surface tension of the crude oil was also determined. Individual surface tensions of two partially miscible or immiscible liquids can be used to analyze the tension at their interface [21]. The IFT was measured by calculating the difference between the surface tensions. Each experiment was performed thrice and average value recorded. Also, contact angles measurement was employed to determine the alteration in wettability between the surface of a solid surface and drop surface [18]. The surface of a measuring cylinder was made oil-wet followed by addition of aqueous dispersion of SDS mediated clay NPs/brine and clay NPs /SDS/brine after which capillary tube was inserted into the mixture to determine the extent of alteration of the surface from oil-wet towards a more water-wet condition. The liquid rise in capillary was determined after each experiment and radius, heights, density of the aqueous mixtures was recorded. The mean values was taken after three repeated readings.

Foam Stability

The foam stability of clay NPs/brine dispersed at constant SDS concentration (8.33 mN/m) was determined by simply hand shaking 20 ml of the mixture in a 100 ml measuring cylinder and visually observing the extent of foam collapse. This was also done for the sol-gel mediated clay NPs/brine. The foam height and stability was investigated at time 0 h, 0.5 h, 2 h, 5 h and 17 h. The foam stability was analyzed to determine the effectiveness of clay NPs/SDS in CEOR.

RESULTS AND DISCUSSIONS

Results of EDXRF (Table 1) showed the elemental composition of Clay NPs in distilled water (NC) and with SDS 2.08 mM (NC-SDS1) and SDS14.58 mM (NC-SDS5). Table 1 shows highest percentage composition of silicon, then aluminium and other minor compositions. This indicates that the KB clay NPs are kaolinite (Al > 16 %; Si > 30 %).

Table 1: EDXRF of Clay NPs

Elements	NC	NC-SDS1	NC-SDS5
Si	30.097	29.832	29.379
Al	16.956	16.192	16.147
Mg	2.090	1.760	2.340
S	0.035	0.195	0.287
Ti	0.805	0.770	0.781
K	0.945	0.931	0.933
Si/Al	1.780	1.840	1.820

The XRD results (Figure 1) show that KB clay NPs in distilled water, 2.08, 6.25, 8.33, 10.42, 14.58 mM of SDS denoted by NC, NC-SDS1, NC-SDS2, NC-SDS3, NC-SDS4 and NC-SDS5) respectively. The XRD confirmed the clay as Kaolinite with two major diffraction peaks at 2θ approximately 21° and 27° that matched with literature pattern [19]. It was observed that these peaks became broadened with reduction in particle size. This trend agree with calculations from Scherrer's formula (Table 2) indicating that as the concentration of SDS increases, the particle sizes decreases from 85 nm to 60 nm for NC to NC-SDS3 respectively. However, there was increase in particles size after NC-SDS3. This suggests that the surface tension of SDS at CMC (8.33 mN/m) gave the least particle size [24].

The surface morphologies of clay NPs were analyzed with SEM and they show platy poly crystallites with more particle aggregations on SDS-mediated clay NPs as compared with NC as shown in figure 2.

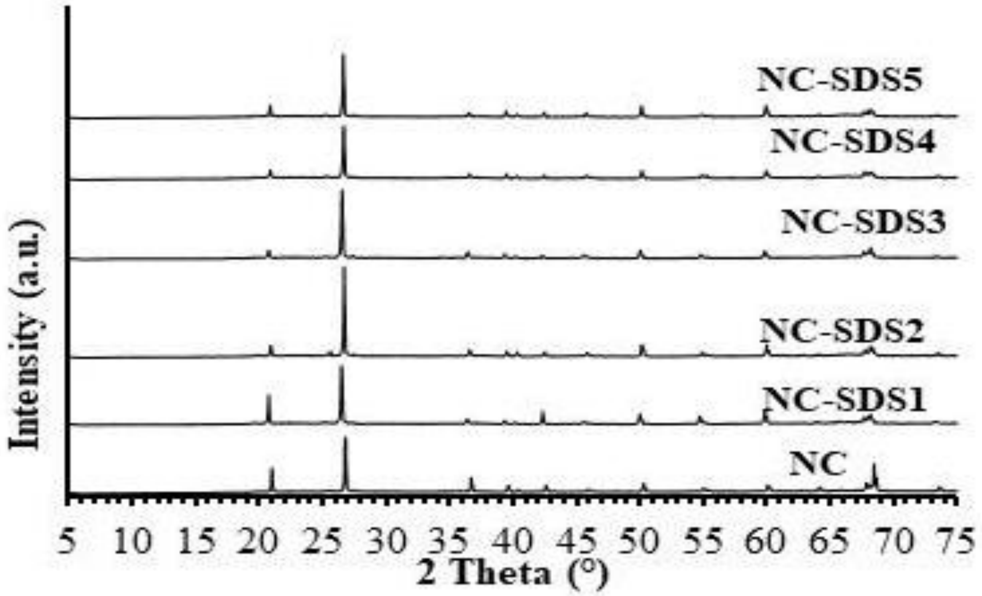

Figure 1: Clay NPs @ varying SDS concentrations (mM)

Table 2: XRD Mean Particle Sizes of Clay NPs

Clay NPs	Mean sizes (nm)	contact angle (°)
BRINE	NIL	86.05
NC	85	81.84
NC-SDS1	63	79.23
NC-SDS2	66	80.51
NC-SDS3	60	78.16
NC-SDS4	66	80.67
NC-SDS5	90	81.97

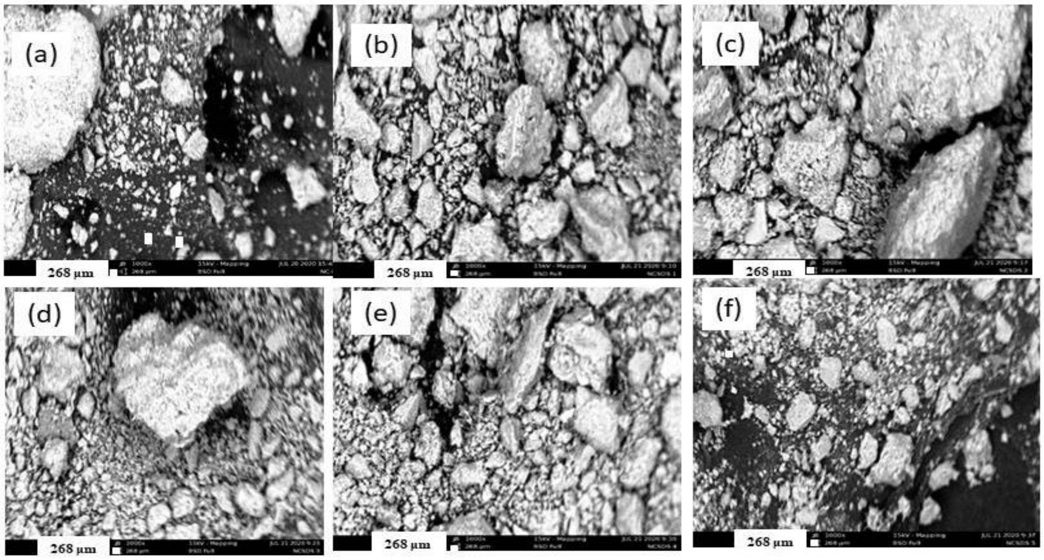

Figure 2: Surface morphologies of (a) NC (b) NC-SDS1 (c) NC-SDS2 (d) NC-SDS3 (e) NC-SDS4 (f) NC-SDS5. (x1000).

This suggests that the exit of SDS solution upon calcination created porous surfaces for the SDS-mediated clay NPs (b-f) resulting to smaller polycrystallites on their micrographs.

The FTIR spectra (Table 3) of the clay NPs showed adsorption bands at 1056, 780 and 3636 cm^{-1} indicating stretching of Si-O bonds and -Mg-O bonds and bending absorption bands at 698cm^{-1} indicating Al-O-H vibrations [23].

Table 3: FT-IR absorption bands for Clay NPs

NC-	NC-SDS1	NC-SDS2	NC-SDS3	NC-SDS4	NC-SDS5	BAND ASSIGNMENT
3655	3555			3636	3655	Al/Mg-O-H Stretching
1056	1056	1052	1056	1056	1052	Si-O Stretching
780	780	780	780	780	780	Si-O Stretching in quartz
698	695	698	698	695	698	Al Al-OH bending

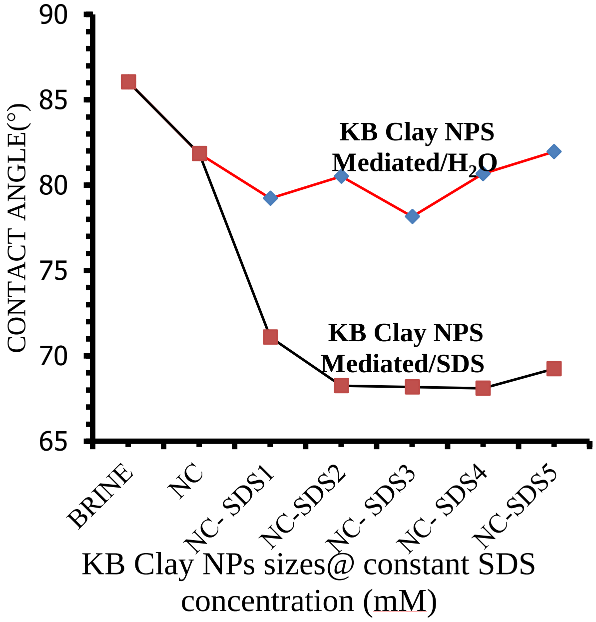

Figure 3: Wettability alteration of Clay NPs (control and with SDS)

Wettability Alteration

The initial wettability changes (Figure 3) shows a neutral–wet condition with brine as contact angle

ISSN 0795 - 22066

of 86.05° for both clay NPs mediated and clay NPs mediated/SDS. With varying particle sizes of clay NPs mediated, little change in wettability was obtained. This was probably due to the calcination of the clay particles with SDS at high temperature causing the carbon bonds and the sulphate groups to be broken [25]. However, for clay NPs /SDS, there was an alteration in wettability as the contact angle decreased indicating an alteration from a neutral-wet towards a water-wet condition (Table 2).

IFT

The effect of clay NPs at SDS concentration of 8.33 mM (Figure 4) shows that IFT between the clay NPs/SDS and crude oil were reduced. The base solution (brine) has a highest IFT value, followed by that of NC, the IFT values reduced to an ultra-low value with the introduction of SDS. This shows mediated clay NPs has little effects on IFT as their carbon bonds have been broken compared to that with SDS where the IFT decreased from 47.67 mN/m to an ultra-low values from 6.02 - 1.98 mN/m at varying clay NPs sizes as similarly reported by [17].

Foam Stability

The variation of clay NPs sizes affects the height and stability of the foam (Figure 5). NC, NC-SDS1, NC-SDS2, NC-SDS3, NC-SDS4, NC-SDS5 gave foam heights of 0, 79, 61, 97, 58, 42 mm respectively. The measured foam height shows that foamability increases with decreasing particle sizes. Clay NPs with the least particle size (NC-SDS3, 60 nm) produced a foam height of 97 mm while NC-SDS5, 90 nm has the least foam height of 42 mm while there was no foam generated with the NC. Also, the particle size variation revealed that NC- SDS3 generated the most stable foam (Figure 6), followed by NC-SDS1 then NC- SDS2 and NC-SDS4. These variations suggest that the relative surface to volume ratio increases foam viscosity thus inhibits film thinning and subsequent liquid drainage. This in turn, retains foam's bulk and bubble stability[22].

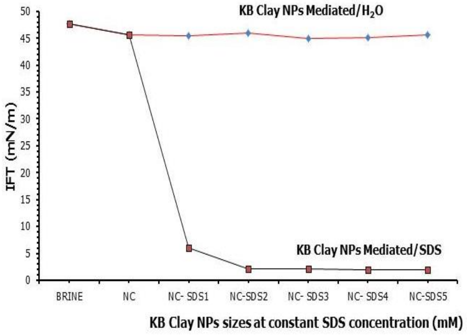

Figure 4: IFT of Clay NPs with varying particle sizes

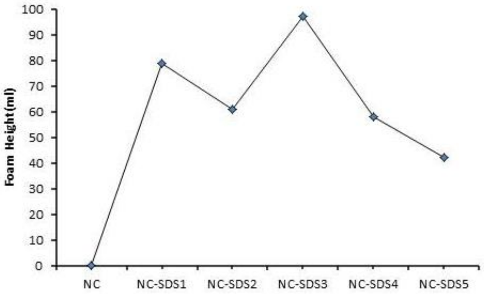

Figure 5: Foamability of Clay NPs with varying particle sizes

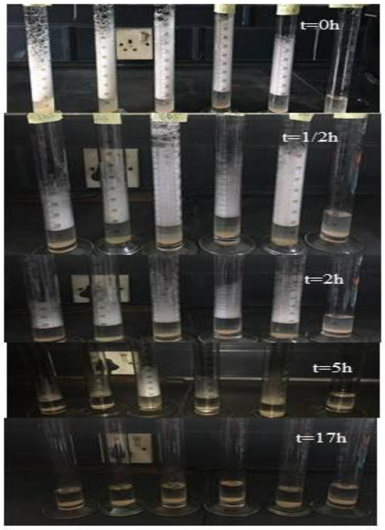

Figure 6: Foam stability of Clay NPs with varying particle sizes

CONCLUSION

SDS-mediated KB clay NPs have been synthesized and characterized for the first time. The foam stability and interactive properties of KB clay in SDS/Brine mixtures have also been studied. The results confirmed that KB clay NPs could serve effectively as alternative to silica. XRD confirmed the KB NPs as Kaolinite while EDXRF showed its alumina and silica contents as Al > 16 % and Si > 30 % respectively. Surface morphologies showed platy polycrystallites of different sizes on the SEM while characteristic vibrations of Si-O stretching (780 and 1056 cm^{-1}) and Al-OH bending (698 cm^{-1}) vibrations were obtained from the FT-IR. Control of particle sizes (85, 63, 66, 60, 66 and 90 nm) was achieved using different concentrations (0, 2.08, 6.25, 8.33, 10.42 and 14.58 mM) respectively of SDS at constant clay particles (10 g) in the sol-gel synthesis. IFT reduction between the oil and the aqueous media at constant SDS concentration increased with decrease in particle sizes from 85 to 60 nm. Similarly, wettability alteration also showed changes from nearly neutral-wet towards more water-wet condition with particle size variation. The foam stability experiment confirmed that the clay NPs with the least particle size of 60 nm gave the most stable foam and should be recommended for CEOR.

Acknowledgements

The authors would like to thank the Tertiary Educational Trust Fund (TETFUND) for providing financial support during this research through Institution Based Research (IBR) Grant (2018) of Rivers State University, Port Harcourt, Nigeria.

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