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Utilizing an Ionic Surfactant for Stabilizing Tungsten Oxide Nanofluids by Reducing Particle Size Distribution

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ABSTRACT

Tungsten oxide nanofluids containing 0.0625, 0.25 and 1% of WO_3 nanoparticles were prepared and characterized. Preparation methodology was based on, homogenization and stabilization of the nanoparticles by ultra-sonic in the presence of cationic surfactant cetyltri methyl ammonium bromide (CTAB) and anionic surfactant sodium dodecyl sulfate (SDS). This treatment was alsoused for increasing the stability and improving the thermal properties of the fluid. Several characterization techniques took a place including measurements of transmission electron microscopy (TEM), particle size distribution and zeta potential and sedimentation photo capturing, physical properties likewise enthalpy, specific heat, entropy and thermal conductivity and, rheology like viscosity, density were used to measure and confirm the stability, sedimentation rate and physical, thermal properties of the prepared nanofluids to be used as cooling material.

Keywords: *Tungstenoxide nanofluid, CTAB, SDS, Thermal properties.*

I. INTRODUCTION

Since 1995 many researchers devoted their efforts to innovate and develop Nano fluids properties and applications. Renewable energy took into consideration as the compatible solution for the future of human. The cooling or heating improvement in an industrial process can save the energy, decrease the time processing, increase the thermal rating, and rise the equipment's lifetime. Nowadays the improving of traditional heat transfer fluids in order to increase the energy efficiency of most of thermal devices and equipment became a key factor to achieve energy conversion in industry. Heat transfer fluids, like water, oil and ethylene glycol are suffering a great heat transfer performance decrease in industrial processes. There is a high interest in development of new forms and types of more effective heat transfer performance for such heat transfer fluids. The use of Nanofluids has shown a better improvement in the thermal properties and enhancements to the thermal efficiency of heat transfer systems, heat exchangers. Nano fluids can be considered as the valuable solution for the difficulties in the thermal engineering science. Nanofluids consists of nano particles homogeneously suspended in dispersing media as long time as possible [1].Efficiency of nanofluid for transfer of heat depends on size of the particles, particle loading percentage, type and surfactant concentration, pH value and Brownian motion[2].The nanofluid heat transfer is so sensible to the thermal properties depending on particles loading percentage. Moreover specific heat capacity (Cp) of nanofluids is the focal point for thermal engineers working on transfer of heat it is used for the estimate balances of energy in the heat exchangers, and pumping power [3-6]. Specific heat capacity Cp decreases with the increasing of nanoparticles loading percentage but increases with the increasing of the temperature [7,8]. Additionally, many studies have accomplished to study the thermal characteristics and thermal properties of tungsten Nanofluids. Sharafeld in et al. [9,10] examined efficiency of the collector with WO_3 in water base fluid and revealed that the solar collectors performance increased by 13.48%, also found that as increasing the loading of WO3 an efficiency enhancement of the evacuated tube solar collector occurred and thermal-optical reached about 72.5%. Nygrenet al. [11] used tungsten as the plasma-facing material and in the development programs for advanced plasma facing components. He et al. [12] measured the viscosity of nanofluid with different nano particle sizes and found that the increase of wt% of nano particles leads to increase viscosity as well as volume fractions of NPs increases. Nguyen et al. [13] achieved that due to increase in Al_2O_3 NPs wt% viscosity of Al_2O_3/H_2O nanofluid authorized significant increase, otherwise viscosity decreases as temperature increase. The current work investigates the use of dual-step method for the synthesis ofWO_3-surfactant/water based nanofluids of different particle loading percentages and different surfactant.

Probe sonication technique used to make good dispersion and reduce particle size. Multiple techniques were applied to characterize and confirm the prepared nanofluids stability and thermo-physical properties.

II. METHOD & MATERIAL

Sodium dodecylsulfate (SDS) (CH_3 $(CH_2)11SO_4Na$), and Cetyltrimethyl ammonium bromide (CTAB) ($C_{19}H_{42}BrN$) were purchased from Oxford (India). Tungsten oxide (99.9%, ACROS Organics, New Jersey, USA) was calcined at 650 °Cfor 4 h.

Nanofluids Preparation

WO_3nanoparticles with different loading weights(0.018, 0.075and 0.3 g) was supported with concentrations 0.0625, 0.25 and 1wt% with30 ml of 1% SDSanionic and 1% CTABcationic base fluid surfactants for stabilization of the nanoparticles dispersion, using deionized water as a fluid [14-16]. The nano particles solutions were homogenized for 15min by ultrasonic to stabilize and homogenize the dispersion of the suspension.

Characterization Techniques

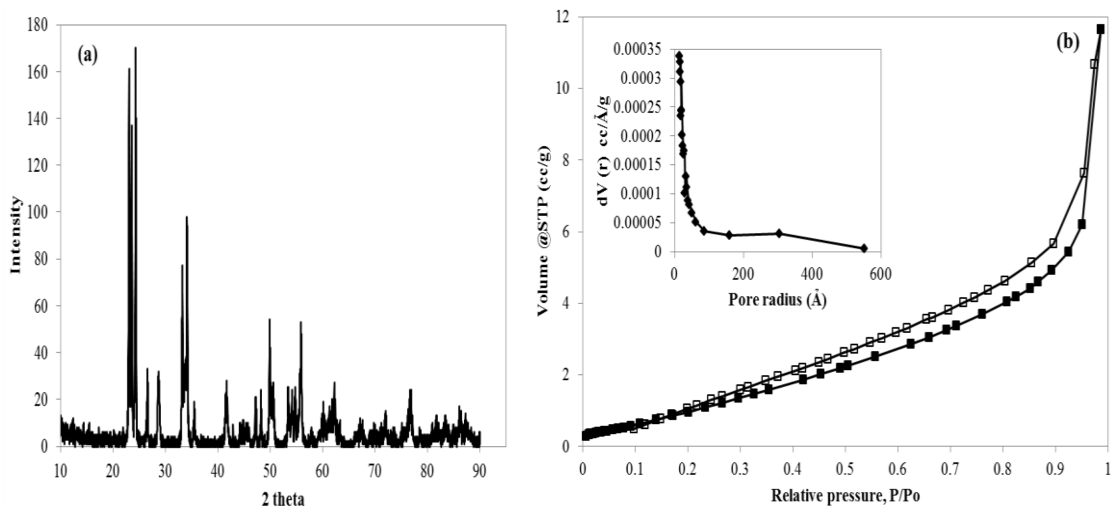
Nitrogen adsorption–desorption isotherms at -196 °C were determined by the aid of a NOVA 3200 apparatus, USA. The powder X-ray diffraction (XRD) patterns were recorded using Shimadzu XD-1 diffractometer (Japan). The morphology of the samples was investigated by the transmission electron microscopy (HRTEM) JEOL JEM -2100 operating at an acceleration voltage of 120 and 200 kV. Average particles size, particles size distribution and zeta potential were measured by using dynamic light scattering (Malvern-ZS) nano-series. The conductivity was measured using portable conductivity meter (FE287). The specific heat was measured by Differential Scanning Calorimetry (DSC) (SDT Q600 TA thermal analyzer USA.). The viscosity and density were measured using PVS TM Rheometer (BOB/STATOR: PVS-B5-D-HC, Cup Type: Hastelloy C).

III. RESULTS AND DISCUSSION

Characterizations of WO_3-nanoparticles

Fig. 1a show X-ray diffraction analysis (XRD) of tungsten according to JCPDS cards no: 0-002-0308, the sharp diffraction lines are assigned to the tungsten oxide. The particle size of WO_3 reached 88 nm according to Scherrer's equation.

Fig. 1b represents the N2 adsorption-desorption isotherm of WO_3, it is belong to Type IV, and the hysteresis loop is of H4 type, according to IUPAC classification. The pore-size distributions (PSD) (inside Fig. 1b), demonstrate that the tungsten oxide possess unimodalpore distribution. The BET surface area is 5.7m^2/gm, pore volume is 0.01788cc/gm, and pore size is 1.57 nm. [17]. The TEM image represents the large cubic-shaped of WO_3nano particles, as shown in Fig. 1. It is evident from the micrographs that the average size of the particles ranges from 40 to 97 nm.



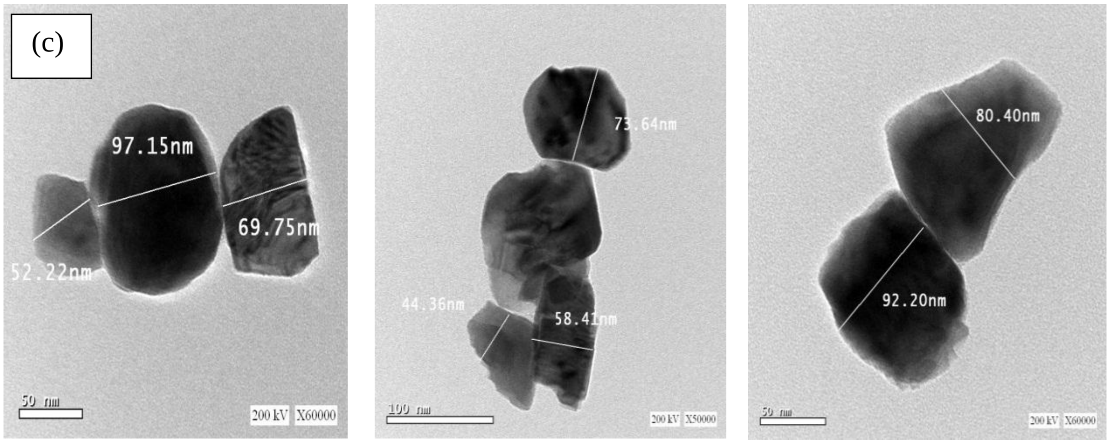


Fig. 1. XRD pattern (a), N2 adsorption-desorption isotherm (b) and TEM image (c) of WO_3 nanoparticles.

Characterization of WO_3Nanofluids

Multiple techniques were used to characterize the synthesized nanofluids samples. Fig. 2 shows the morphology of nanofluids synthesized with CTAB and SDS as stabilizers. The surfactants were used to keep the particles stable and uniformly suspended in the basefluid. As shown in HRTEM images for WO_3/SDS nanofluid tungsten oxide particles were dispersed due to the electrostatic repulsive force between the surfactant surface and the nano particlesIn the case of WO_3/CTAB nanofluid, a well-defined thin surfactant around the nanoparticles can be observed.

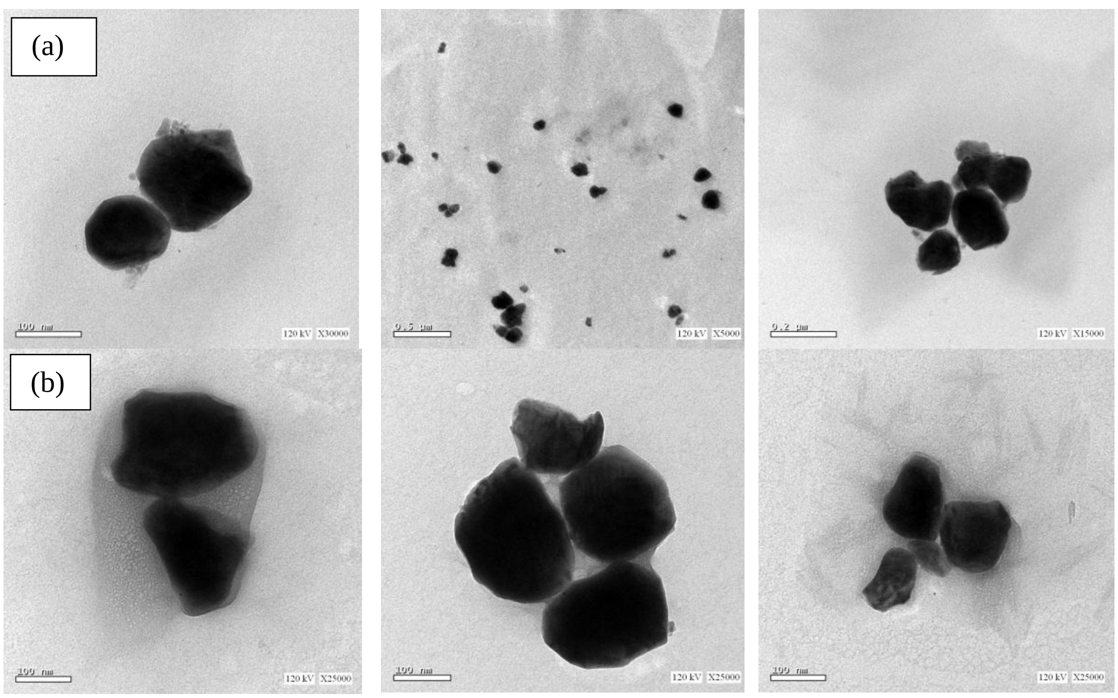


Fig. 2. TEM images of WO_3/CTAB (a) and WO_3/SDS (b) nanofluids

Zeta Potential and Particle Size Distribution of Tungsten Nanofluids

Average particles size, particles size distribution and zeta potential were measured using dynamic light scattering (Malvern-ZS) nano-series. The average particle size of synthesized nanofluids is given in Table 1. The particle size decreases gradually as tungstenoxide nanoparticles concentration increases from 0.0625% to 1% with the constant of 1% surfactant especially in the case of anionic surfactant because it has high ionization degree in water which cause high repulsion force between the nanoparticles.

Table 1. Average particle size (nm) of the prepared nanofluids

WO_3 %	**0.0625**	**0.25**	**1**	1% WO_3/H_2O
Average particle size of WO_3/SDS, nm	69.29	42.07	38.9	111.90
Average particle size of WO_3/CTAB, nm	72.16	71.4	56.98	

The small particle size in case of WO_3/SDS nanofluid system is according to the deployment of surfactant charge on the nano particles surface, electrostatic repulsive force took a place on the particles surface leads to separate and disperse the particles so a good dispersion occurred without aggregate formation[18]. On the other side the larger particle size in the case of WO_3/CTA Bnano fluid system is according to the surrounding of surfactant around WO_3nano particles as showed in TEM picture so increasing the particle size was detected. However, Fig. 3 shows that the use of SDS surfactant decreased the average size aggregation in comparison with the use of CTAB and H_2O.

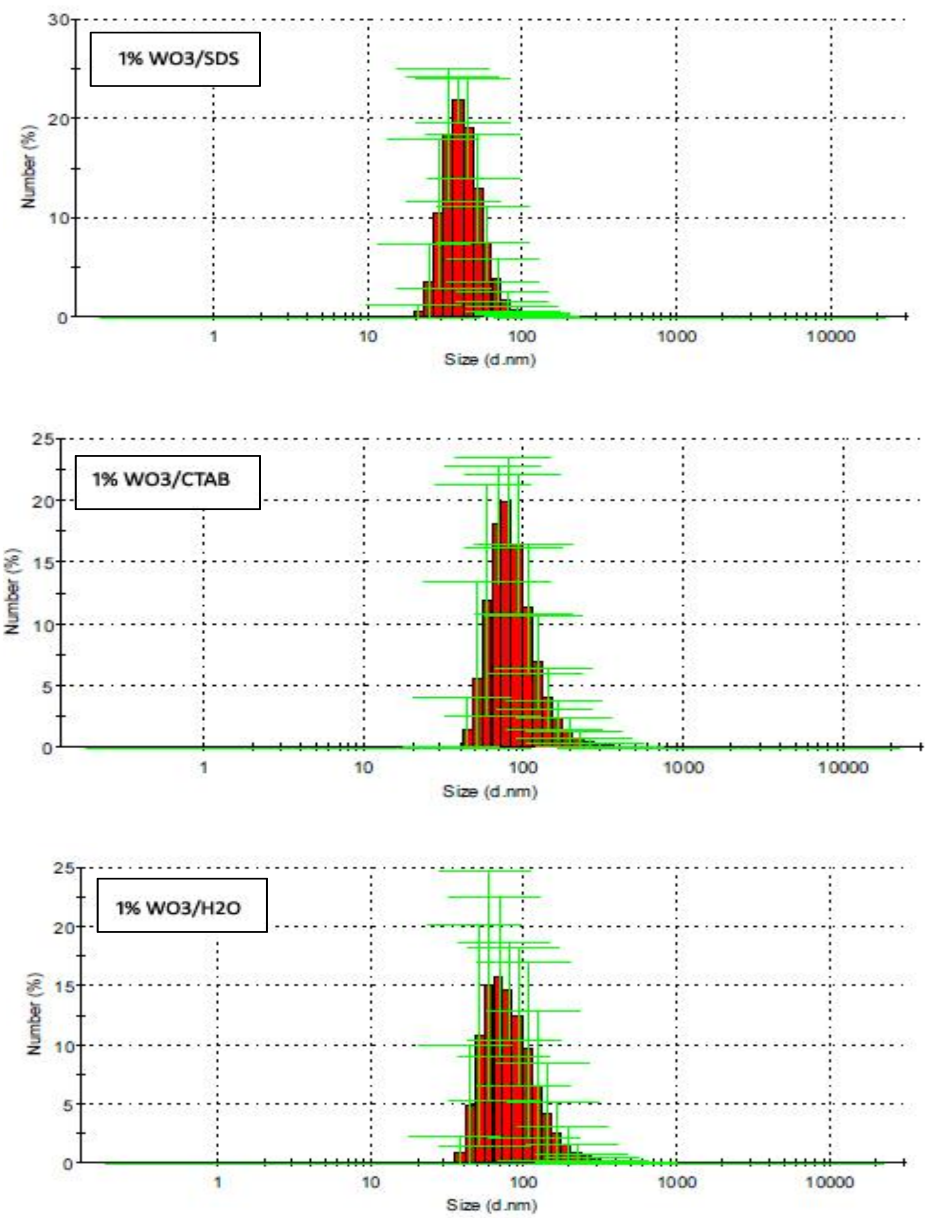


Fig. 3.Aggregate size distribution of the prepared nanofluids

Zeta potential measurement is one of the techniques to evaluate the stability of Nano fluids. Assessing the stability by the zeta potential index is related to the electrostatic repulsion forces between the nanoparticles. When the repulsion is high, it can be concluded that the nanoparticles collisions will be low. Therefore, the nanofluid can be classified as a stable one. Generally; nanofluids consider stable when the measured zeta potential is greater than 30 mV [19, 20].Fig. 4 shows that thezeta potential of tungsten oxide nanoparticles is -27.9 mV but it reached to -60.5 mV, 42.2 mV-44.3mV for WO_3/SDS, WO_3/CTAB, and WO_3/H_2O nanofluids. This revealed that the addition of anionic surfactant increases the stability of nanofluids more than the cationic surfactant and H_2O, again the nanofluids system is highly disturbed and tend to stabilize according to electrostatic repulsion forces by distribution of ions and formed electrical double layer on the surface of nanoparticles. This was confirmed from the constant values of zeta potential with time, as illustrated in Table 2.

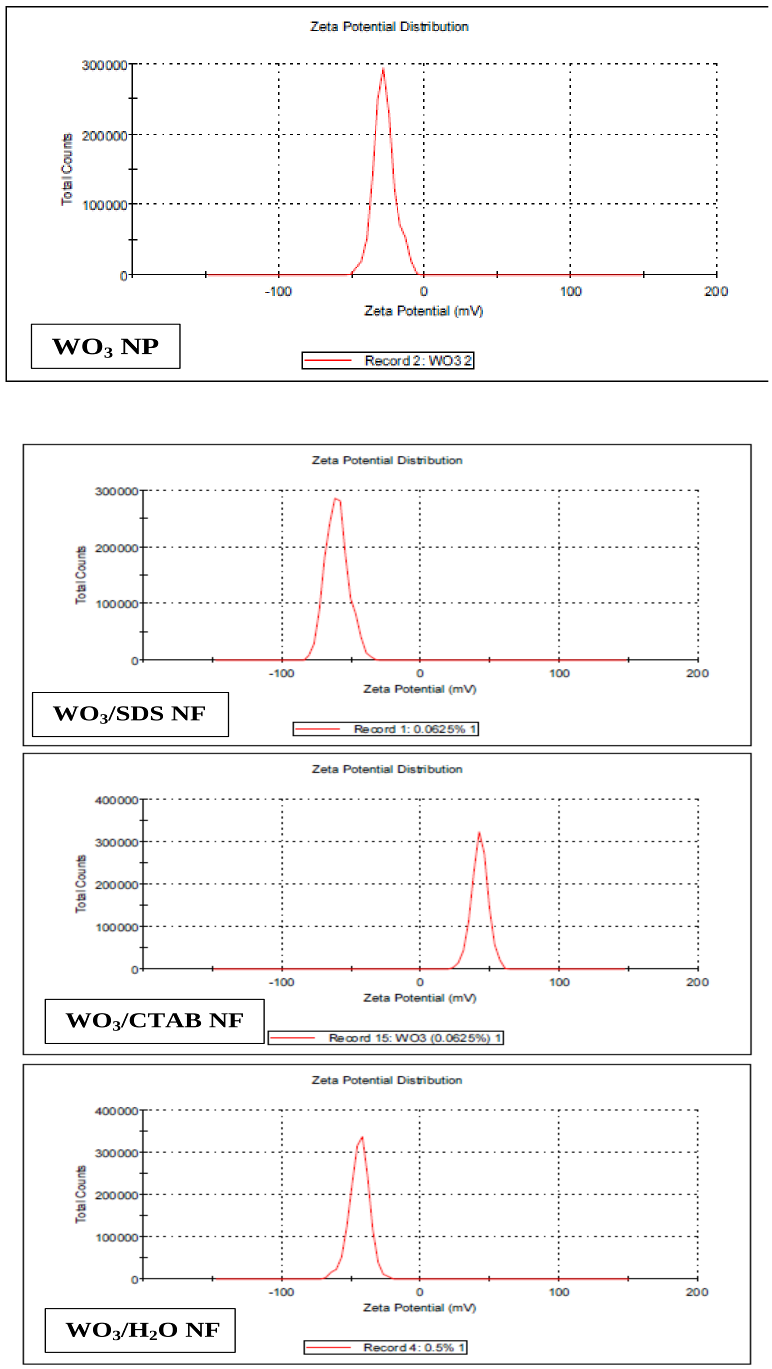


Fig. 3 Zeta potential of the prepared nanofluids

Table 2: Zeta potential values of the prepared nanofluids

Time (min)	WO_3/CTAB	WO_3/SDS
0	-0.211	0.563
60	38	-53.5
120	42.1	-59.3
180	42	-60.9
240	42.2	-60.5

Stabilization of Tungsten oxideNanofluids

The stability of WO_3/CTAB nanofluidswithWO_3 loading percentages of 0.0625, 0.25 and 1wt% were tested with time. The results showed that the freshly prepared nanofluids with low WO_3 concentration after the period of 4, 7, 15, 21, and 30 days respectively. As shown in Fig. 4 the particles have a tendency to settled after 21 days due to the attraction force between negative charge of nanoparticles and positive charge of CTAB which increasing agglomeration and sedimentation with time. Fig. 5 shows the photo capturing of freshly synthesized WO_3/SDS nanofluids with WO_3loading percentages of 0.0625, 0.25 and 1 wt% at 4, 7, 15, 21, and 30 days respectively. Visually, the WO_3/SDS nanofluids show valuable stability over an extended period of time, due to the ability of SDS to undergo ionization which increases both the dispersion and entropy of the solutions.

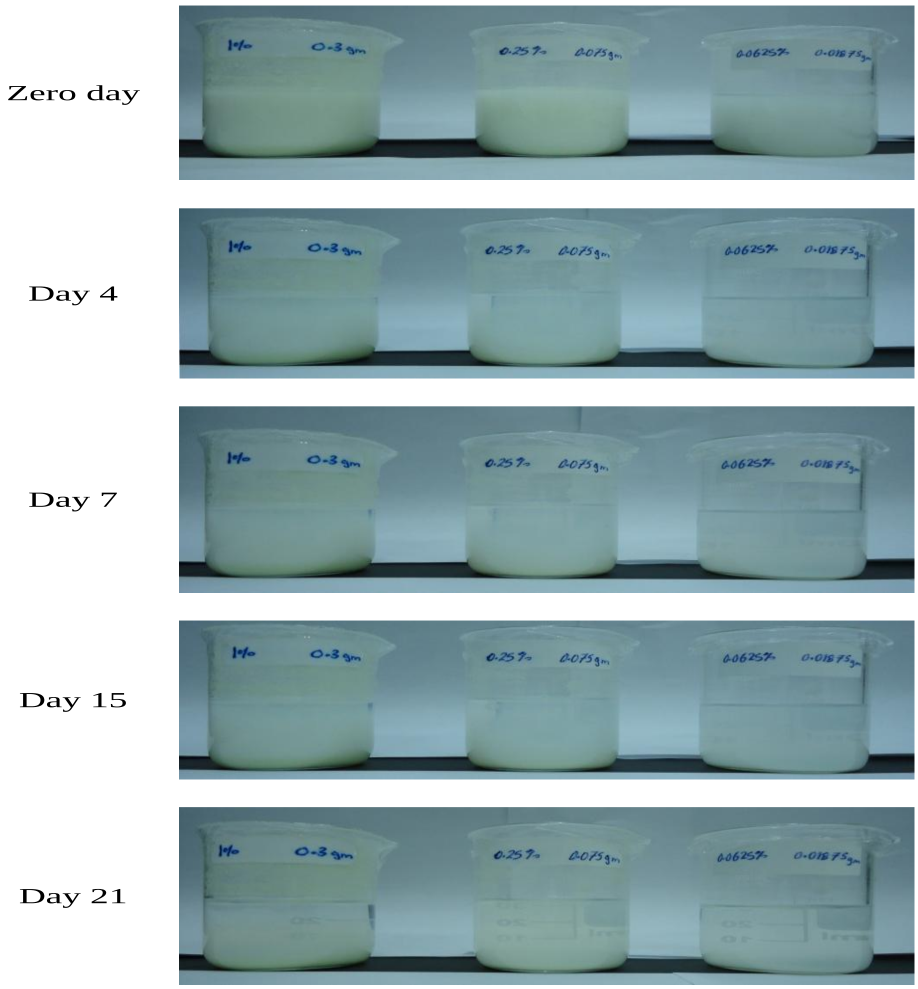


Fig. 4. Stability assessment of WO_3/CTAB nanofluids

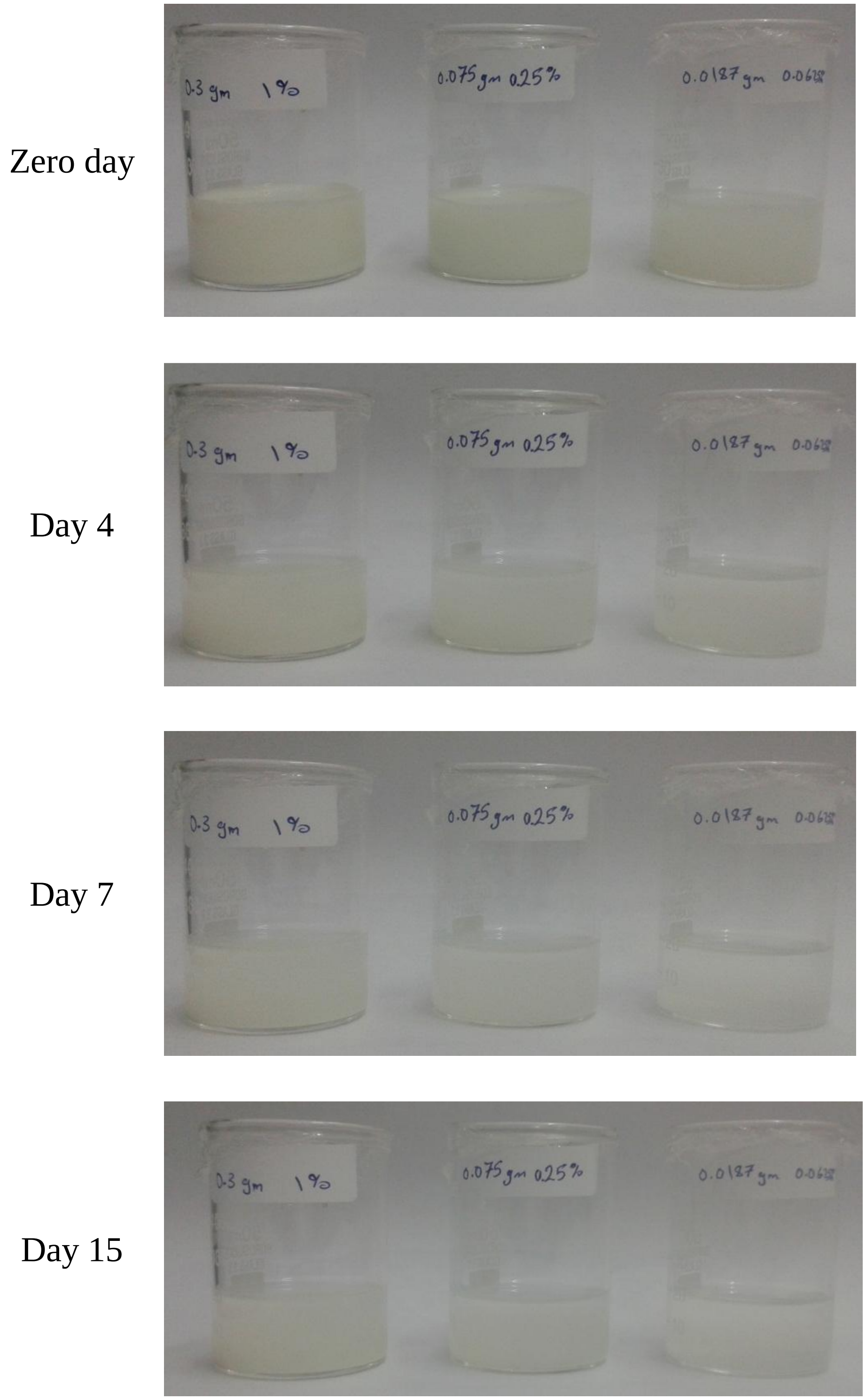


Fig. 5. Stability assessment of WO_3/SDS nanofluids

The effect of time on particle size distribution can be seen in Figs.6&7 For three different concentrations of WO_3/CTAB and WO_3/SDS nanofluids respectively. The particle size of WO_3 nanofluids remained constant within10 days for all WO_3loading percentages, according to addition of surfactants which increase the nanofluids stability[21].

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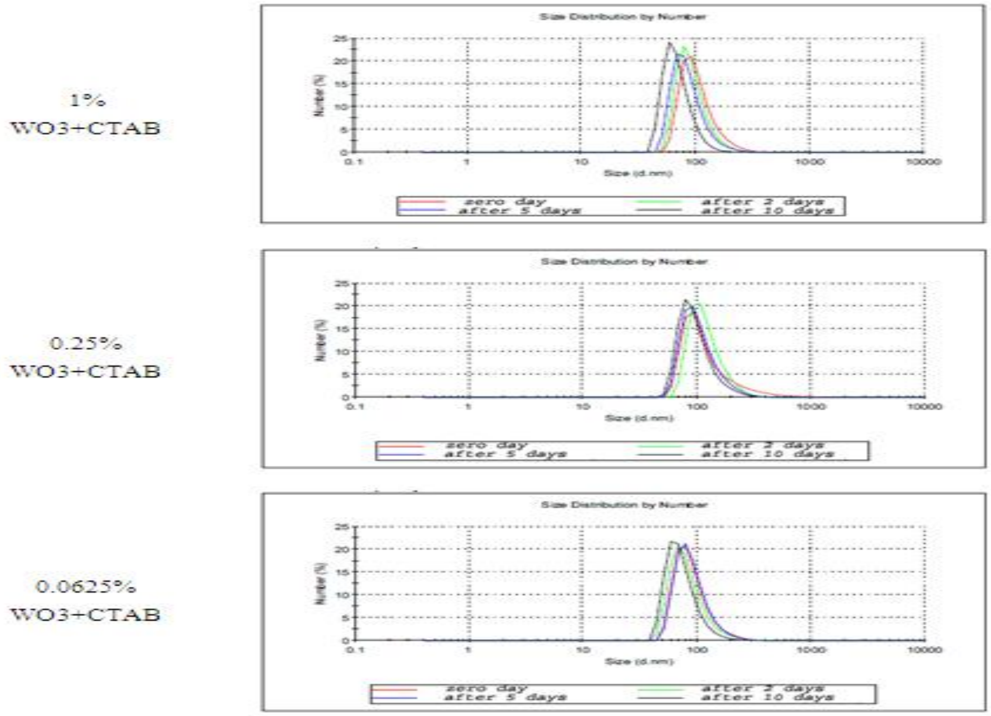

Fig. 6. Particle size distribution of different concentrations of WO_3/CTAB nanofluids at time intervals; zero time, after 2days, 5days up to 10 days measured by dynamic light scatterings (DLS)

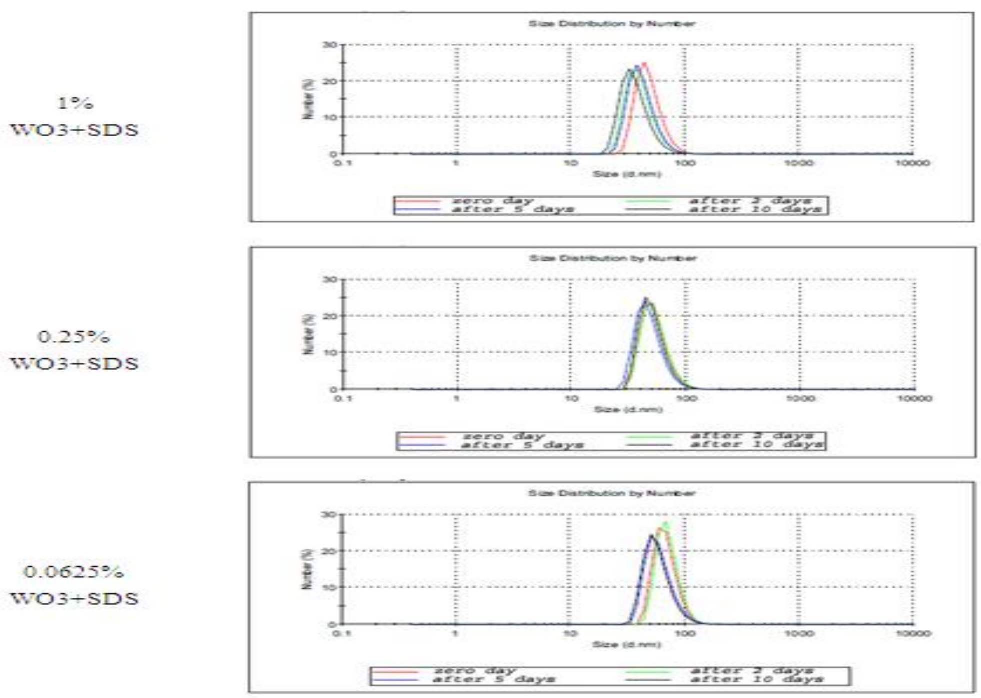

Fig. 7. Particle size distribution of different concentrations of WO_3/SDS nanofluids at time intervals; zero time, after 2days, 5days up to 10 days measured by dynamic light scatterings (DLS)

Physical Properties of Tungsten Nanofluids

The most important property that can be scrutinized to prove the enhancement of the synthesized nanofluid heat transferis the thermal conductivity. A dramatic enhancement of the conductivity occurs with adding small loading percentages of tungsten oxide [22-24]. Fig. 8 shows the thermal conductivity variation of tungsten oxide nanofluids with temperature from 30 °C to 60 °C. Addition of WO3nano particles to both surfactant basefluids enhanced the thermal conductivity with a magnificent value in comparison to water basefluid. The maximum thermal conductivity value reached 433mS/cm for 1%WO3/CTAB nanofluidat 60 °C. Under these conditions, the pH ofthe prepared nanofluids I s4.55(Table 3). Wang et al. [25] reported that the addition of surfactant tonano particles lowers thepH value of the fluids and the charge on the surface decreases the particles repulsion as seen in DLS results with cationic surfactant. Therefore, the increase in the thermal conductivity classified.

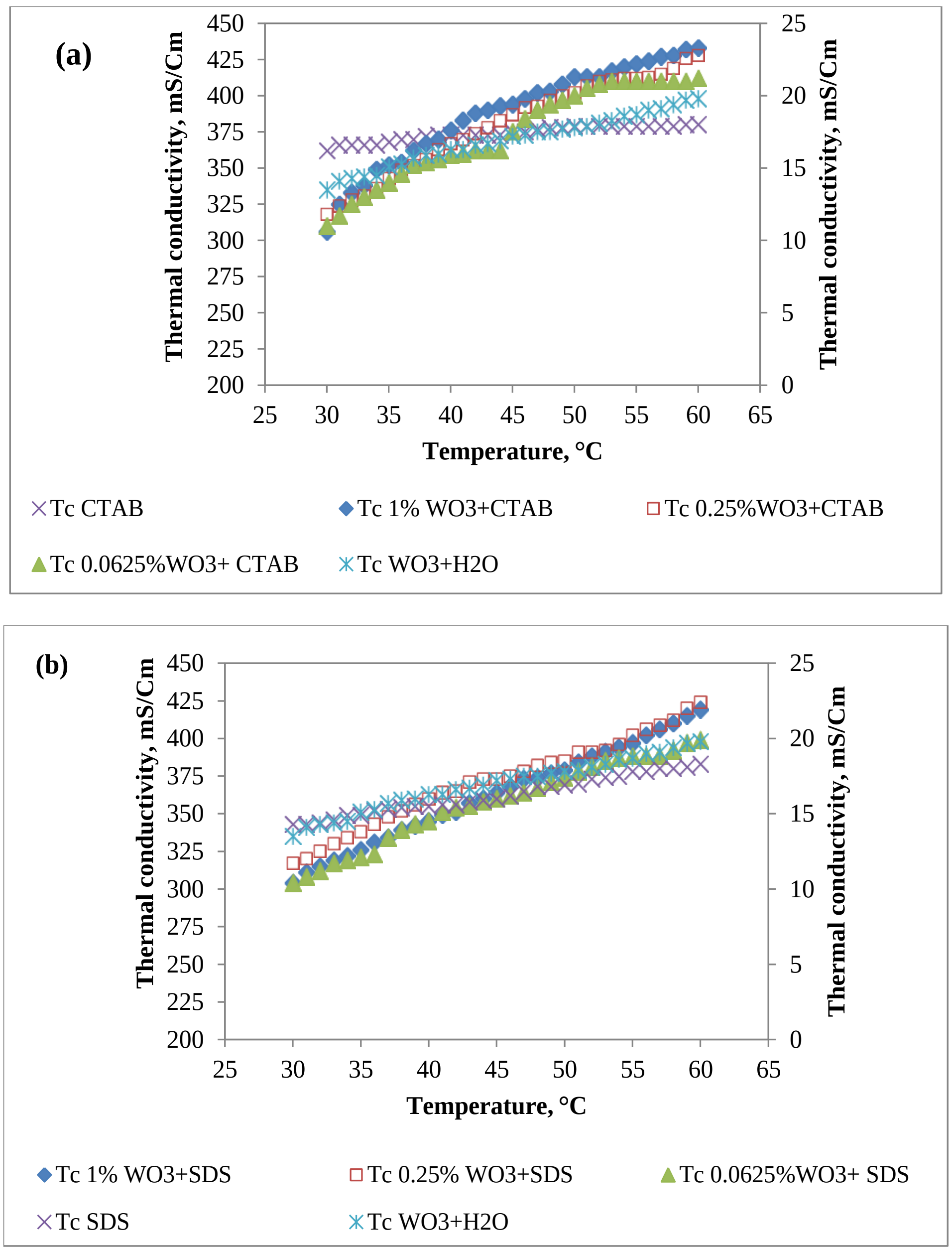

Fig. 8. Variation of thermal conductivity with temperatures of WO_3/CTAB (a) and WO_3/SDS (b) nanofluids

According to study of Yang et al. [26], it is clarified that the main parameters that effect on the viscosity of nanofluids are the interaction between surfactant and nanoparticles besides the dispersion type. Viscosity has been measured for different volume fractions, increasing in viscosity observed as the volume fraction increased as illustrated in Table 3. [27].The CTAB base nanofluids showed lower viscosity values in comparison with SDS and water base fluids. Density of the prepared tungsten oxide nanofluidsis directly proportional to the volume ratio or the concentrations of nanoparticles. It's consequence to the higher density of solids than liquids. This is compatible with previously published results [28].

Table 3:Physical properties of tungstenoxide nanofluid

WO_3%	0.0625	0.25	1	1% WO_3/H_2O	
PH					
SDS	7.25	6.30	5.81	5.29	6.77
CTAB	5.55	5.42	4.55		5.71
Dynamic viscosity at 25 °C					
SDS	364.30	365.10	365.90	631.40	627.00
CTAB	357.00	361.40	365.70		618.30
Density (g/cm^3) 25 °C					
SDS	1.000	1.001	1.002	0.9524	0.9576
CTAB	0.9855	1.002	1.003		0.9626

Fig. 9 shows the change of heat flow at constant pressure against the temperatures range of 14 °C -250 °C to measure the specific heat, WO_3/CTAB and WO_3/SDS nanofluids using DSC technique, according to the following expression [29]:

$$C_p = \frac{\Delta H}{\Delta T}$$

Where Cp is the specific heat at constant pressure, ΔHis the enthalpy and ΔT is the difference between T2 and T1. According to the third law of thermodynamic, the entropy (ΔS) of nanofluids can be calculated, according to the following equation:

$$\Delta S = 2.303\, Cp \log\left(\frac{T_2}{T_1}\right)$$

The results show that the entropy of WO_3/SDS nanofluids is higher than that of WO_3/CTAB as illustrated in Table 4, this consequence with the degree of ionization of SDS surfactant

Table4. Thermophysicalparameters of the preparednanofluids

Fluids	ΔH (Jg^{-1})	C_p ($J.°C^{-1}$)	ΔS ($J.°C^{-1}$)
WO_3/CTAB	2130	12.85	28.15
WO_3/SDS	2324	13.50	33.84

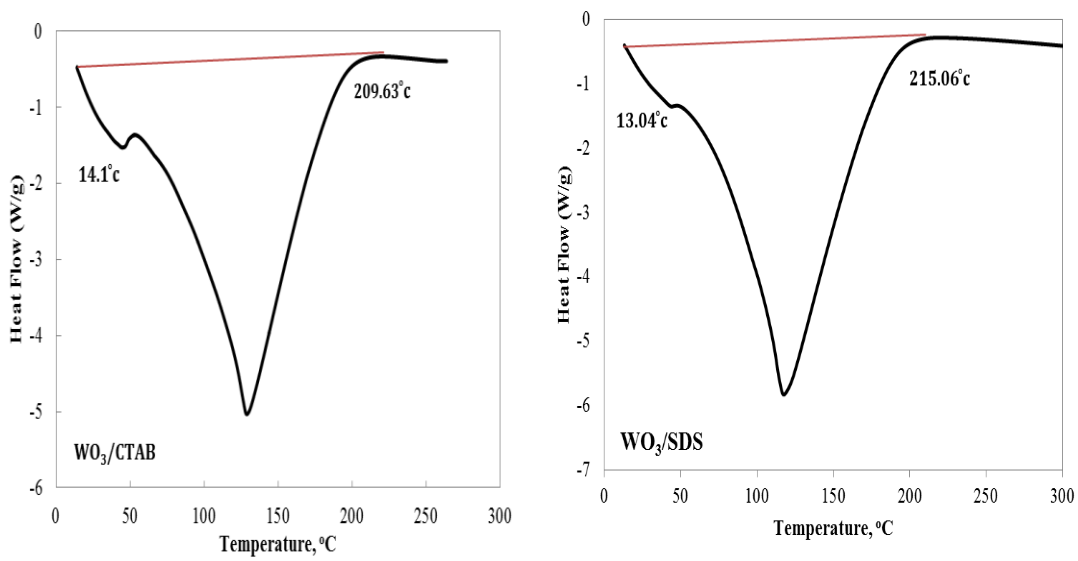

Fig.9. Change of heat flow with temperature of the prepared nanofluids

IV. CONCLUSION

A series of tungsten oxide nanofluids was synthesized in the concentrations of 0.0625, 0.25 and 1 wt% using both CTAB and SDS surfactants of 1% as stabilizing agent. Multiple techniques were utilized for stability study, sedimentation rate and physical property for prepared nanofluids. TEM showed a good dispersion of nano particles in the surfactant basefluids. Zeta potential of WO_3/SDS,WO_3/CTAB and WO_3/H_2O, systems was found to be -60.5 mV,42.2 mV and-44.3 mV respectively. Capture photo for all WO_3 concentrations showed that the WO_3/CTAB nanofluids were stable within the 21, whereas the WO_3/SDS nanofluid showd valuable stability over an extended period of time, due to the ability of SDS to undergo ionization which increases both the dispersion and entropy of the solutions. The maximum value of thermal conductivity reached 433mS/cm and 424mS/cm for 1%WO_3/CTAB and 1%WO_3/SDS nanofluids at temperature of60 °C.

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