Optimization Efficiency of Nano Emulsion Surfactants as Base Oil Antioxidants and Anti-wear Additives

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

Original Research Article

ABSTRACT

N-hexadecyl-N-benzyl-N-methylglycine and N-Dodecyl-N-benzyl-N-methylglycine were studied as antioxidants and anti wear. The physico-chemical properties were investigated; the adsorption behavior of these compounds at oil interface was investigated by measuring the surface tension and interfacial tension as function of concentration. Surface properties, in particular the critical micelle, the maximum surface excess and the minimum surface area were measured. It is found that the surface and thermodynamic properties of the prepared surfactants depend on their chemical structure. Also it is found that there is a good relation between surface properties of the additive and their efficiency as antioxidants. The mechanism of the antioxidation action has been suggested according to the surface properties of each additive. Adsorption of the additive on the surface interface inhibits their free radicals trapped in micelle core. These compounds were added to oil in different concentrations. The antioxidants activities of different dosages were evaluated. The oxidation of the oil has been carried out for different time intervals. The degradation of the oil has been monitored by total acid formation. The anti wear characteristic of surfactants increase with increasing hydrocarbon chain length. This is due to the increase in chemisorptions of surfactants on the silicon carbide surface. These films provide lower wear and depend on amount

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of surfactants concentration adsorbed on silicon carbide and sliding speed. These studies have led to determine the effect of adsorbed surfactants in dispersion of nano particles of silicon carbide in oil phase. The anti wear characteristic of surfactants increase with increasing dispersed silicon carbide. These studies have led to much clear evidence of the intimate relationship between the chemical structure of the surfactants and dispersed silicon carbide.

Keywords: Additives; anti wears; surfactants; base oil Introduction.

1. INTRODUCTION

Micro emulsion is formed when water is dispersed in a hydrocarbon based continuous phase and is normally located towards the oil apex of a oil/surfactant. In this region, thermodynamically driven surfactant self-assembly generates aggregates known as reverse or inverted micelles, which minimize surface energy, is the most common form. Added amphoteric surfactants will become compartmentalized into the central cores of these reversed micelles, hence affording fine dispersion of inorganic materials in oil. Any inorganic reagents encapsulated inside the micelles will become mixed. This exchange process is fundamental to nano particle synthesis inside reversed micellar, allowing different reactants solubilized in separate micellar solutions to react upon mixing. Micelles in these systems can be described as "nanoreactors", providing a suitable environment for controlled nucleation and growth. In addition, at the latter stages of growth, steric stabilization provided by the surfactant layer prevents the nano particles from aggregating.

Nano structured materials, often characterized by a physical dimension (such as particle size or grain size) of less than 100 nm, attract much interest due to their unique properties compared to conventional materials.

The author studied different additives as pour point and anti oxidants [1-3]. On the other hand, other additives were prepared by phase transfer catalysts, like S-phenyl thioglyconitriles with other derivatives [4-7]. Novel method of inhibiting oxidation was suggested elsewhere [7-9]. Therefore, it is very important to choose the correct additives and optimize their concentrations, to get best efficiency.

The author prepared P-decyloxy p-sodium sulphonate azobenzene with chemical structure $H_{21}C_{10}O-Ph-N=N-Ph-SO_3Na$ and 1- ethyl-1-dodecyl-2-sulphonate -4- (hydroxyl ethyl)-piprazine and evaluated as additives in metalworking fluid for anti-corrosion and anti-oxidant. The author suggested the field of action mechanism of the additive according to its surface properties.

Some amphoteric surfactants N-Decyl-N-benzyl-N-methylglycine and N-Dodecyl-N-benzyl-N-methylglycine were prepared. The physicochemical characteristics were investigated. The adsorption behavior of these surfactants at oil/air interface was investigated by measuring the surface tension and interfacial tension as function of concentration. Surface properties, in particular the critical micelle concentration (CMC), the maximum surface excess (Γ_{CMC}) and the minimum surface area (A_{min}) were measured. It is found the surface and thermodynamic properties of the prepared surfactants depend on their hydrocarbon chain length. Also it is found that there is a good relation between surface properties of the additive and its efficiency in depressing the pour point. The mechanism of the depressants action has been suggested according the micelle of each additive [7]. Adsorption of the additive on the surface of the wax particles inhibits their growth and alters the crystal habits through micelle core. The surface and thermodynamic parameters confirm the suggested mechanism and the decreasing of pour point. This is resulted in a multilayer, more isotropic wax crystal, and thus only a fixed amount of wax separates at any given temperatures. The results were discussed in terms of adsorption isotherm.

In the present study addition of silicon carbide and titanium oxide to lubricating oil in the presence of N-hexadecyl-N-benzyl-N-methylglycine and N-Dodecyl-N-benzyl-N-methylglycine as emulsifier used to obtain the effect of load, sliding speed, sliding time on wear rate against sliding with carbon steel.

2. EXPERIMENTAL

Preparation the additive by phase transfer catalysts in two techniques:

N-Dodecyl-N-benzyl-N-methylglycine(C_{12}) and N-hexadecyl-N-benzyl-N-methylglycine(C_{16}) were synthesized early [7]. 3 mol of N methyl benzylamine and 1 mol of calcium chloroacetate react overnight in pure ethanol at 50C° in the presence of 0.1 mol of benzyl triethanol ammonium chloride as phase transfer catalyst. The resulting solution was treated with sodium carbonate and recrystallized by alcohol. The product was calcium salt of N-Dodeecyl-N-benzyl-N-methylglycine(C_{16}) and N-Hexadecylecyl-N-benzyl-N-methylglycine(C_{12}).

Surface tension of different concentrations for 10^{-7} to 0.1 mol/L of the synthesized additives was measured by using Kruss Model 8451 in petroleum ether at 30C° according to omar et al. [10].

The physicochemical properties of the base oil are listed in the following Table [7]:

Properties	Base oil	Test
Density (g/ml) at 15.5 C	0.8958	D. 1298
Refractive index nD^{20}	1.4955	D. 1218
ASTM color	4.5	D. 1500
Kinematic viscosity cSt		
at 40 C	17.56	D. 445
at 100 C	29.15	D. 455
Pour point C	15	ASTM D 97
Molecular weight	520	GPC
Total paraffinic content , wr%	59.353	Urea adduction [7]
Carbon residue content, wt%	1.9	ASTM D524
Ash content, wt%	0.0511	ASTM D482

2.1 Preparation Si C Nano Particles

The sample silicon carbide calcined at 500 C, crushed and sieving to nano particles. Then mixed with silicon carbide in the presence of different concentrations of additives and evaluated. The modified oil was evaluated by measuring its wear resistance, oxidation stability. The oxidation test was carried out at 120C° according to ASTM D 943 standard methods. The base stock sample was subjected to oxidation with pure oxygen at a flow rate of 0.1 L/hour for maximum 70 hours. Wear tests were carried out using Pin-on-ring apparatus under sliding speed of 300, 350, 400 and 450 rpm in wet conditions at room temperatures. The samples have the form of cylindrical shape with 8 mm diameter and 12 mm long. During the test, the sample was passed against stainless steel ring with normal load of 5 N. Test duration 10

minutes for each sample. Wear of the sample was measured by its weight loss [3].

3. RESULTS AND DISCUSSION

Detailed physical- chemical characteristics of the paraffinic oil are reported in the above table. The prepared compounds were confirmed by author early [7].

The surface tension decreases with increasing the compound concentrations. The difference between them is attributed to hydrocarbon group of each molecule (C_{12}, C_{16} groups). The action of additive can be calculated using Gibbs adsorption equation [10,11]. Comparing the data in Table 1 shows that the CMC value for the compound (C_{16}) was lower than that of the compound (C_{12}), which indicates that the former C_{16} favors micellization processes at a lower concentration than the latter compound. Studying the results in Tables 1, 2 shows that, the synthesized amphoteric surfactants C_{16} has large values of surface excess and minimum surface area, indicating the C_{16} is the most efficient and gives a greater lowering in surface tension of oil. Thus the change in hydrocarbon group of (hydrophobic part) affect the degree of micellization which will be the reflect of efficiency of the additive and of its activity in oil phase. These results confirm that the compound $C_{16 is}$ more soluble and more active in oil phase. These results are compatible by the author (7). Thermodynamic parameters of micellization (standard free energy, ΔG_{mic}, standard entropy change, ΔS_{mic} and standard enthalpy change, ΔH_{mic} of the prepared surfactants were calculated according Omar et al. [10]. ΔG_{mic} values are negative indicating that the processes of micellization processes is a spontaneously depend mainly on the hydrocarbon chain length (Table 2). ΔS_{mic} is positive reflect degree of random and increased upon transformation of one methylene group of the molecule of surfactant from the interface to the bulk of micelles. The degree of randomness increased by increasing the temperature. On the other hand ΔH_{mic} values are positive due to the endothermic process of amphoteric salvation upon micellization, These results are compatible with our results published early [7].

Thermodynamic parameters of adsorption (standard free energy, ΔG_{ads},, standard entropy change, ΔS_{ads}, and standard enthalpy change, ΔH_{ads}) for amphoteric surfactants have more negative values than those corresponding to the

micellization processes. This indicates that the adsorption process of surfactant molecules is more energetically favored and these molecules act as free before micellization.

The prepared additives are adsorbed on nano particles of silicon carbide as shown in Fig. 1.

The adsorption isotherms of the prepared surfactants were determined at 25C. The sample was carefully prepared and the size fraction was shifted to nano particles with surface area 58.5 m^2gm^{-1} for the adsorption measurements. One gram of silicon carbide was stirred in 50 ml of the surfactant in oil for 3 h. The amount of adsorbed was calculated from the total concentration and equilibrium concentration of free surfactant. The adsorption isotherms obtained for two prepared surfactants (C_{12}, C_{16}) adsorbed by silicon carbide are presented in Fig. 1. The adsorption densities shown are based on cross – sectional areas of 18, 20 A^{02} for surfactants C_{12} and C_{16}respectively. It is clear that the adsorption density increased with the surfactant concentrations. The adsorption density amounts 57% to 60% respectively.

The effect of this additive on the oxidation stability of oil is given in Figs. 2, 3. The data show that the additive retards the oxidation of oil for limit time and loss its efficiency after 50 hours. Comparing between two additives in increasing oil stability, the additive C_{16} is the best; due to it has the best surface properties. The author concludes that the ability and stability of micelle is predominant factor for increasing oxidation stability of oil. The micelle inhibits propagation of free radicals and terminates reaction processes of free radicals as discussed early [2-8]. It is clear that additive adsorbed on the metal surface forming thin film.

3.1 Anti-wear Properties

The additive forms a film between the metal surface and the rotating ring that minimize the wear rate. Figs. 4, 5 show the best anti wear additiveC_{16}. With increasing the sliding speed to 600 rpm, the worn surface seems rougher compared to other worn at 300 rpm, the worn surface was totally damage. On the other hand addition of different concentrations of each additive at constant speed 400 rpm lead to increase wear resistance and the efficiency of C_{16} additive is preferable than C_{12} (Fig. 5). This behavior is due to the dependence of inhibiting efficiency on the surface area of the additive.
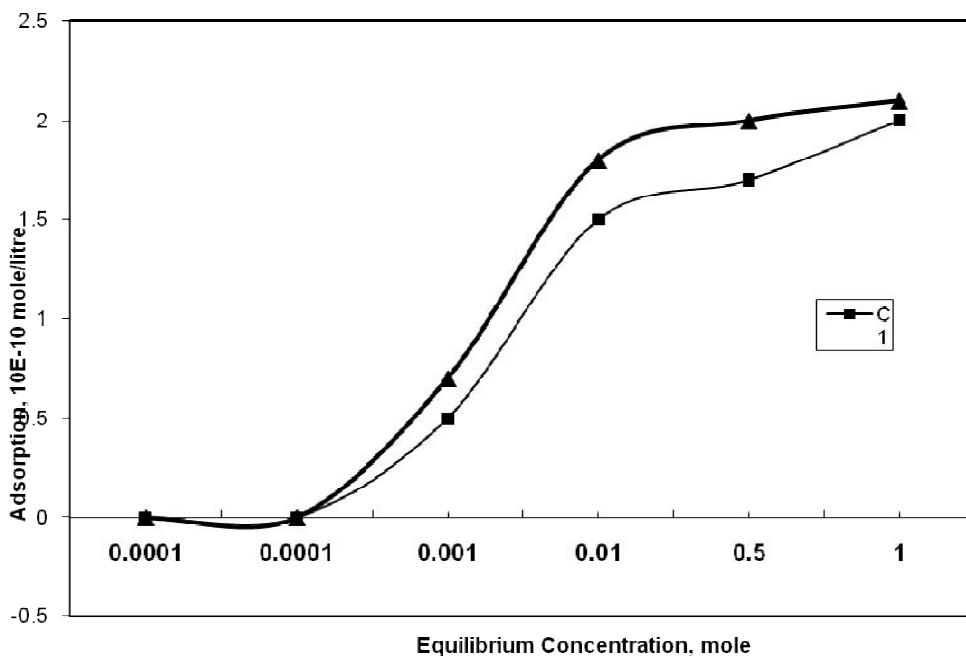

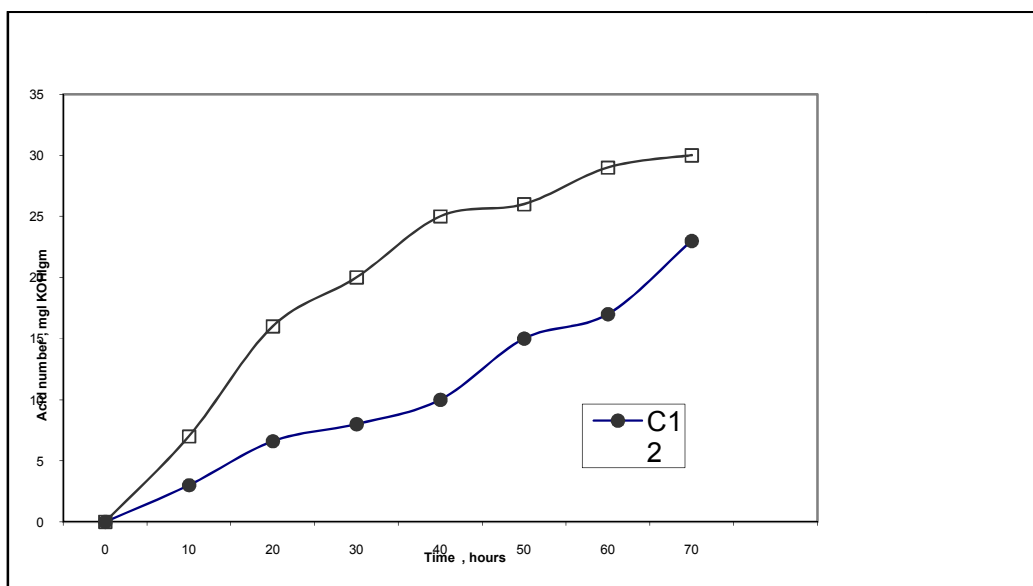**Fig. 1. Adsorption isotherm of additive on silicon carbide**

Fig. 2. Effect of concentrations of two additives of on acid number
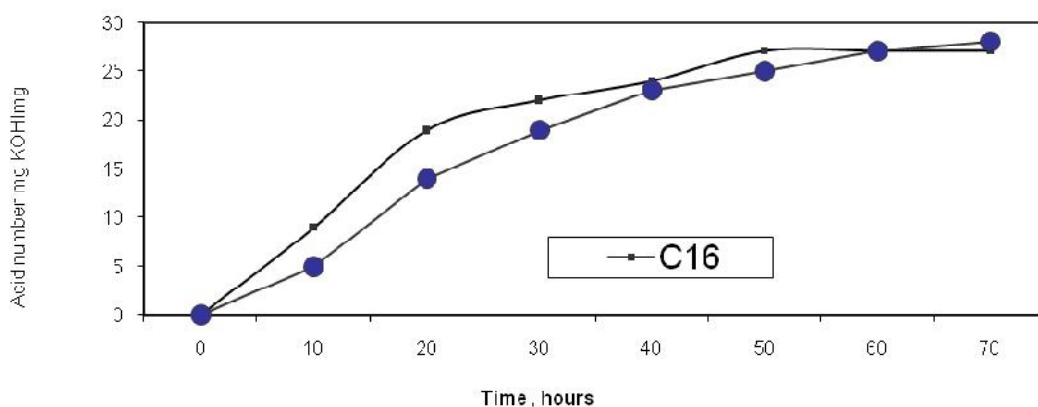

Fig. 3. Effect of hydrocarbon chain lenth of the additive on total acid number at constant concentration 0.1g/L

Table 1. Surface properties of two additives at 25C

Critical surface tension Mn/M^2	Γ_{max}x10^3 mol/cm^2	A_{min}x10^{2}nm^2	-log (CMC)	T, C^0	Compound
18	8.7	48.5	2.25	25	C_{12}
12	9.5	98	3.01	25	C_{16}

Table 2.Thermodynamic parameters of additives at different temperatures

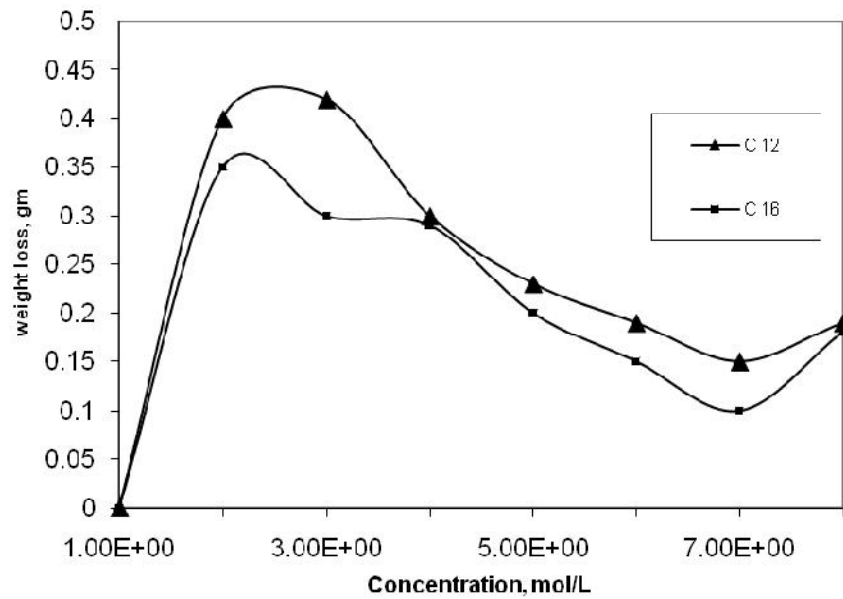| ΔH_{ads} KJ/MOL	ΔS_{ads} KJ/MOL	ΔG_{ads} KJ/MOL	ΔH_{mic} KJ/MOL	ΔS_{mic} KJ/MOL	ΔG_{mic} KJ/MOL	T, C^0	Compound
5.2	0.02	-12.5			-12.2	20	C_{12}
		-14.76	4.9	0.06	-13.1	25	
		-15.2			-16.2	20	C_{16}
8.7	0.01	-18.5	-9.72	0.07	-18	25	

Fig. 4. Effect of additive concentration on wear resistance at spead 400 rpm at constant condition
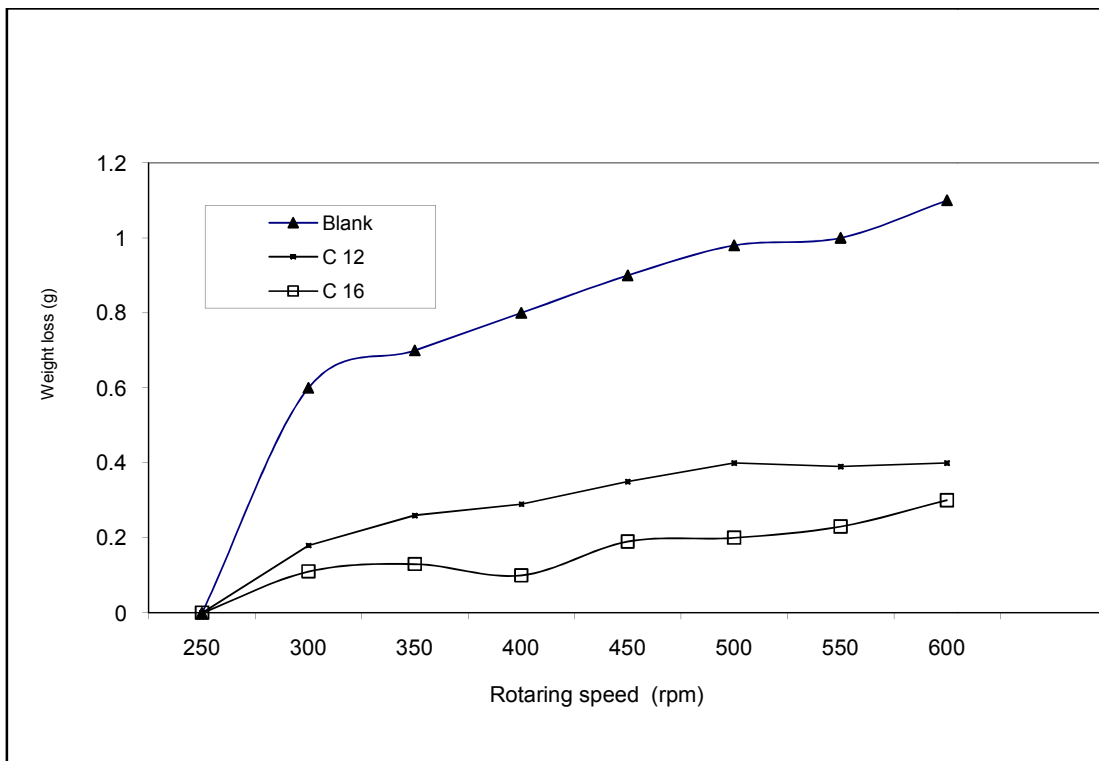

Fig. 5. Effect of rotaring speed and additives on wearing using lube oil

4. CONCLUSION

1- The results strongly indicate that the anti-wear and antioxidants effectiveness of all additives depends on hydrocarbon chain length, concentration, silicon carbide and sliding speed.
2- 1-The oxidation stability of oil as measured by total acid number indicates that, the oxidation inhibitor efficiency follows the order

$C_{16} > C_{12}$. These results are depend on silicon carbide at oil phase.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=893&id=7&aid=7880