New Trend in Enhancement Quality and Pour Point of Waxy Gas Oil by Nanoemulsions Part-1

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Abstract— *Hydrocarbons are organic compounds consisting of hydrogen and carbon. There are many sub-groups: paraffins, such as alkanes, alkenes, alkynes, naphthenes, such as cycloalkanes, and aromatics, such as xylene and benzene, as well as many other related compounds consisting of hydrogen, carbon, nitrogen and sulphur. A wide variety of hydrocarbon components are blended together to make fuels according to the specifications appropriate for cars. In this research, nanoemulsions are prebared , with droplet size on the order of 100 nm. A typical nanoemulsion contains oil, water and an emulsifier prepared by phase transfere catalysts. The addition of an emulsifier is critical for the creation of small sized droplets as it decreases the interfacial tension i.e., the surface energy per unit area, between the oil and water phases of the emulsion. The emulsifier also plays a role in stabilizing nanoemulsions through repulsive electrostatic interactions and steric hindrance. This research focus has been on preparing nanoemulsions through phase transfer catalysts .The physic chemical characteristics were studied. The adsorption isotherm behavior of these emulsifiers was investigated by measuring the surface tension and interfacial tension as function of concentration. It is found that there is a good relation between surface properties and quality of gas oil. Also, the results indicating that more stable emulsion can improve pour point and high quality of gas oil. The results are discussed according the surface properties and thermodynamic parameters of emulsifiers and nano emulsion. The author suggests new mechanism foe enhancement gas oil instead mild visbreaking gas oil in presence of hydrogen gas. This method has many advandage in compare with visbreakig methods.*

Keywords— ***Synthetic fuels, Nanoemulsions, Phase transfere catalysts.***

I. INTRODUCTION

Microemulsions are stable emulsions are stable emulsions of hydrocarbons and water in the presence of surfactants and co-surfactants. They are characterized by spontaneous formation, low interfacial tension, and thermodynamic stability. They have high solublization capacity for both hydrophilic and lipophlic compounds. Surfactants used are petroleum sulphonates and ethoxylated alcohol sulphates, The degree of interfacial tension lowering depends on the phase behaviour of the oil/water/surfactant mixture (1-4).

Some ester is widely used as lubricants and high performance industrial fluids. They are characterized by good biodegradability, low volatility, good lubricity, good thermal stability and low pour points. Ester oils are now used in many applications including automotive engine oils, hydraulic fluids, and compressor oils. The structure of the sorbiton palmitate (SPT) was confirmed by I.R spectrum, NMR, and by mass spectroscopy and studied elsewhere (5,6). The molecular weight was depicted and confirmed by mass spectroscopy(4). On the other hand the physical properties of the mixed system of anionic/ nonionic surfactant and its efficiency in pour point depression were studied early (3). The modification of the lyophobic and lyophilic groups, in the structure of the surfactant, may become necessary to maintain surface activity at a suitable level. Action mechanism of sorbitan palmitate as multifunction additive (4). The efficiency of this additive depends on its critical micelle concentration. The properties of aqueous solution of single component surfactant can be modified by mixing with another compatible one. 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 their efficiency in depressing the pour point (6). The structure of the mixed micelles is expected to be identical to that of single component micelles. Hence, critical micelle concentration of the mixed system can be deduced theoretically based on the initial composition of each component (7,8).The mechanism of the depressants action have been suggested according the micelle of each additives. Adsorption of the additive on the surface of the wax particles inhibits their growth and alters the crystal habits through micelle core. As the results 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

The aim of this work is evaluate the mixture of sodium salt of poly alkylated diphenyl ether sulphonat as anionic surfactants (ANS) and nonyl phenol ethoxylate with a mean of 10 ethoxy units per nonyl (ETH) which prepared elswhere as wax / water emulsifier (4,9,10).These emulsions act pour point depression for base oil. The author study the effect of different mole fractions of the additives on degree of pour point depression, and suggest the field of action mechanism of the additives according to micelles.

II. EXPERIMENTAL

The diphenyl ethers was alkylated by the Friedel-Crafts reaction from diphenyl ether and 1- bromododecane in the presence aluminum chloride and 0.1 gram of tetraehylammonium bromide as phase transfer catalyst. Then, the product was sulphonated and neutralized to produce sodium salt of poly alkylated diphenyl ether sulphonat according Omar et al (9,10). It was found that their physical properties were varied by changing the lengths and number of alkyl groups added to the aromatic rings .The degree of purity about 98% with following chemical formula:

C_{12} $H_{25}C_6H_3$(SO3Na) OC_{12} $H_{25}C_6H_3$(SO3Na).The nonyl phenol ethoxylate with a mean of 12 ethoxy units per nonyl (ETH) was prepared by reaction of nonyl phenol and ethylene oxide (9,10). Into several 100 ml beakers, portion of a given concentration of (ANO) solution (0.01 mol/L) were placed, followed by addition of a given concentration of (ETH) solution (0.01 mol/L). The mixtures were diluted stepwise with water. These mixtures were stirred for 30 minutes in a thermostat at 30^{0}C in order to establish their equilibration. The surface tension of aqueous solution of single and/or mixed surfactant system were measured at 30 ^{0}C using Du Nouy tensiometer (KRUSS Type 8451).

Nanemulsion were prepared in two step: firstly, a pre-emulsion was prepared by addition of water in different percentage (2, 4, 6,8,10 and 12 wt%) to a mixture of ANS and ETH compounds. with constant stirring at 600 rpm. In second step, the prepared pre-emulsion were stirred at high 1000 rpm for 15 min. All experiments were run at 30 C^0.

The physicochemical properties of the base oil are listed in the following table:

Properties	Base oil	Test
Denisty (g/ml) at 15.5 C	0.8958	D. 1298
Refactive index nD^{20}	1.4955	D. 1218
ASTM colour	4.5	D. 1500
Kinematic viscosity cSt at 40 C at 100 C	16.56 28.15	D. 445 D. 455
Pour point C	18	ASTM D 97
Molecular weight	520	GPC
Total paraffinic content , wr%	22.353	Urea adduction
Carbon residue contenty, wt%	1.9	ASTM D524
Ash content, wt%	0.0511	ASTM D482

Pour point depression performance of compound ANS and ETH was evaluated with gas oil by pour point according to ASTM-D 97.

III. RESULTS AND DISCUSSIONS

The variation of surface tension of the air/solution interface as a function of concentration of prepared compounds ANS and ETH is given in Table 1 and Fig. 1. It is clear that the surface tension decreases more with increasing the compound concentrations. The difference between them is attributed to functional group of each molecule (hydrophilic group). Using the Gibbs relation, the action of additive including the maximum adsorption density at the air/ solution interface and area occupied/ molecule can be calculated (11,12). Comparing the data in Fig. 1 shows that the CMC value for the compound (ANS) was higher than that of the compound (ETH), which indicates that the former ETH favors micellization processes at a lower concentration than the latter compound. Studying the results in Table 1, shows that, the synthesized surfactants ANS has large values of surface excess and minimum surface area, indicating the ANS is the most efficient and gives a greater lowering in surface tension of oil with more emulsion stable. Thus the change in hydrophilic group of (hydrophobic part) affects of degree of micellization and emulsion stability. Also table (2) shows the emulsion stability of ETH and ANS in seconds at 30C. The results confirm the compound ANS is more efficient than compound ETH at different volume of water. Increasing the sulphonate group increase the emulsifying power. This is due the ANS adsorbs at the interface and lower surface tension between oil and water. Therefore, when mixed ANS and ETH that have different solubility in water. The critical micelle of mixtures decrease according to the mole fraction of addition (Table 3) and surface tension decrease as shown in Fig 2. This is compatible with published elsewhere by Omar (13). This means that the two compounds ANS and ETH arrange with more stable micelle at the interface and decrease repulsion force between the micro emulsions particles.

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 (11,12) as shown in table 4. These parameters enhance micellization processes and adsorption of additives at the interface. As the results the stability of emulsion increases and the mixture of ANS/ETH prefer of forming stable emulsion due to decrease the interfacial tension between oil and water (Fig.2). These results is combatable with published elsewhere (6,7) . These parameters confirm that the stability of emulsion depend on thermodynamic parameters and value of critical micelle concentration. These value of cmc depend on degree of mixing ANS/ETH (mole fraction). From Table 3 increase mole fraction of ANS/ETH from 0 to 0.7 lead to minimum cmc, then stat to increase with increasing percentage of ETH. These results compatible wih published elsewhere (6,7). ΔG_{mic} values are negative indicating that the processes of micellization processes is a spontaneousity depend mainly on the hydrophilic sulphonate or ethoxylate group, while ΔS_{mic} are positive reflect degree of random On the other hand ΔH_{mic} values are positive due to the endothermic process of anionic or non ionic surfactants in micellization processes. This indicates that the adsorption processes of surfactant molecules is more energetically favored and these molecules act as free before micellization which compatible with published elsewhere by authour (6, 7)

A the results, we predict the activity of these surfactant reach maximum at CMC at mole fraction 0.7 ANS/ETH. This value has the critical surface tension (Fig 2). Furthermore,. So below CMC the surface tension represent the critical value for adsorption and it activity of free molecules of surfactants (Table 3).

It can be conclude that, the activity of the additive in oil phase enhances by mixing of ANS with ETH and the values of CMC. This is due to the fact the micellization processes increase and act as core or trap for fine particles of oil.

The investigation of the ability of additives as pour point depressant in Table 5,6 . It is clear that, the pour point is improved by increasing the additive concentration. The optimum value for reduction pour point obtained at 0.0008mole/L. It is represented the critical micelle concentration. The addition of ANS to ETH forms a mixture exhibiting better performance in reducing pour point as shown in table 6 . As discussed early, addition of non ionic ETH surfactant to anionic ANS lead to lowers the cmc and critical surface tension. These results are compatible with surface properties of additive; i.e. Surface excess concentration of mixture increase with increasing of mole fraction , until 0.7 of ANS/ETH. The author suggests the sulphonate group solublize the wax while the ethoxylate group act as shelding between wax particles. As the results, disperse wax crystal lattice to small sizes, consequently the pour point decrease.

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Table.1: Surface properties of additives at 30C⁰

Additives	**CMCmol/L.10⁴**	**Surface excess concentrations $\Gamma_{max}^{x\ 107}$ mol/m2**	**Area occupied per molecule nm²**
ANS	5.2	7.5	0.66
ETH	3.8	5.6	0.45

Table.2: Effect of water percentage % on stability of microemulsions at 30C⁰by ETH and ANS

% of water in nanoemulsions	**ANS Stability, Time , Sec.**	**ETH Stability, Time , Sec.**
2	150	140
4	160	150
6	200	200
8	260	230
10	220	210
12	180	170

Table.3: Surface properties of additives at different mole fractions ANS/ETH

Mole fraction	**CMCmol/L.10⁶**	**Surface tension at CMC mN/m**	**Area occupied per molecule nm²**
0.2	3.8	22	3.5
0.4	3.1	20	3.8
0.6	2.5	18	5.5
0.7	1.5	12	8.6
0.8	2.5	15	5.5

Table.4: Thermodynamic parameters of additives at 30 C

Compound	**T, C⁰**	**ΔG_{mic} KJ/MOL**	**ΔS_{mic} KJ/MOL**	**ΔH_{mic} KJ/MOL**	**ΔG_{ads} KJ/MOL**	**ΔS_{ads} KJ/MOL**	**ΔH_{ads} KJ/MOL**
ETH	30	-15.1	0.06	5.9	-16.76	0.02	5.8
ANS	30	-20.5	0.07	-8.72	-18.9	0.01	10.5

Table.5: Effect of different additives on pour point at different concentrations

Adittive	**Conc mollL**	**Pour point , C**
ANS	0.00005	**10**
	0.00008	**7**
	0.00009	**5**
	0.0005	**1**
	0.0008	**4**
ETH	0.00005	**12**
	0.00008	**9**
	0.00009	**9**
	0.0005	**7**
	0.0008	**5**

Table.6: Effect of different mole fractions of ANS/ETH on pour point 1% of water in nanoemulsions.

Adittive	**Mole fraction**	**Pour point , C**
ANS/ETH 5% of water in nanoemulsions	0.2	8
	0.4	5
	0.5	4
	0.7	-1
	0.8	4
ANS/ETH 8% of water in nanoemulsions	0.2	9
	0.4	7
	0.5	6
	0.7	1

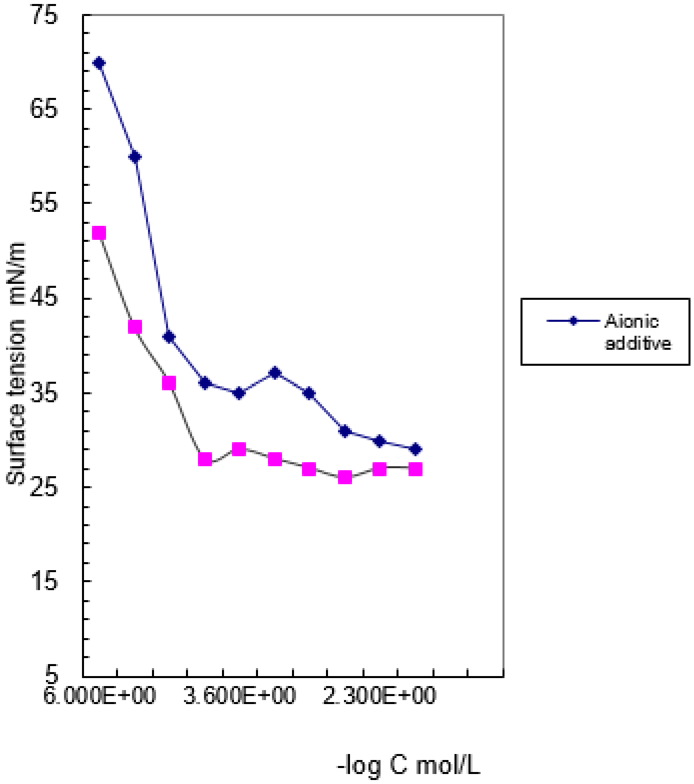

Fig.1: Effect of additive concentrations on surface tensions.

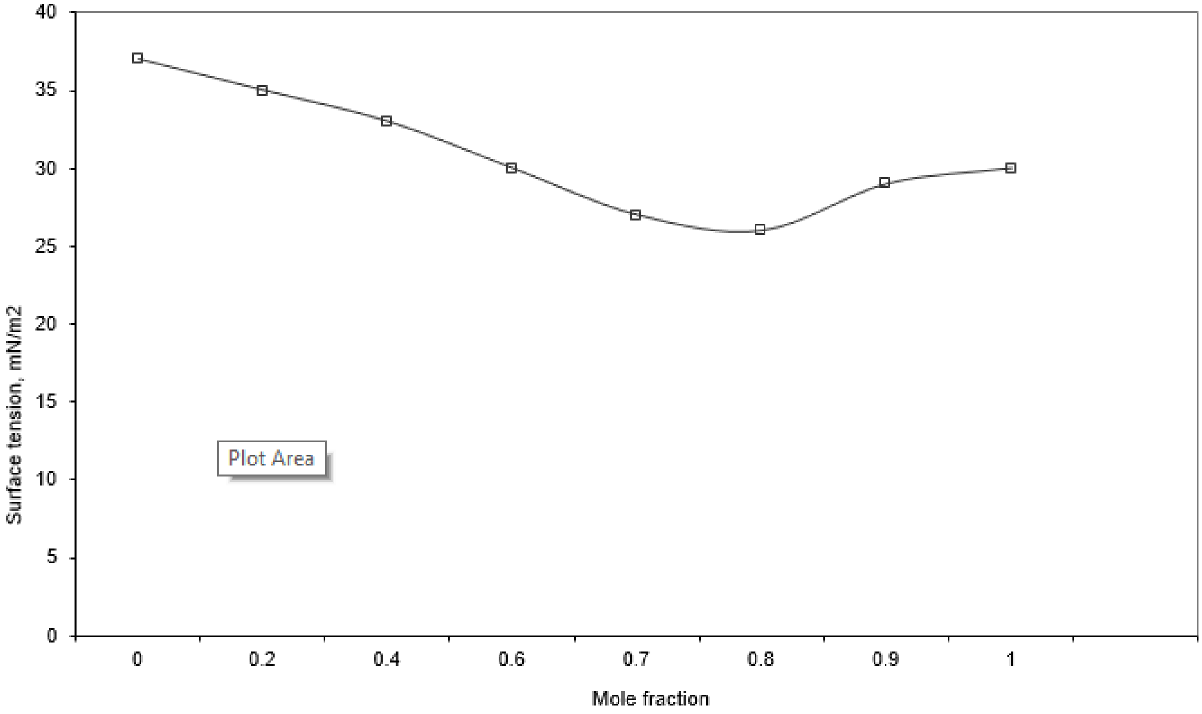

Fig.2: Effect of different mole fractions of the prepared additive on surface tension at solution/ air interface