Retraction Notice

Retraction initiative (multiple responses allowed; mark with **X**):
X All authors
☐ Some of the authors:
☐ Editor with hints from   ○ Journal owner (publisher)
                               ○ Institution:
                               ○ Reader:
                               ○ Other:
Date initiative is launched: 2020-1-3

Retraction type (multiple responses allowed):
☐ Unreliable findings
   ○ Lab error   ○ Inconsistent data   ○ Analytical error   ○ Biased interpretation
   ○ Other:
☐ Irreproducible results
☐ Failure to disclose a major competing interest likely to influence interpretations or recommendations
☐ Unethical research

☐ Fraud
   ○ Data fabrication   ○ Fake publication   ○ Other:
☐ Plagiarism   ☐ Self plagiarism   ☐ Overlap   ☐ Redundant publication *
☐ Copyright infringement ☐ Other legal concern:

☐ Editorial reasons
   ○ Handling error   ○ Unreliable review(s)   ○ Decision error   ○ Other:

X Other: Request from the Author.

Results of publication (only one response allowed):
☐ are still valid.
X were found to be overall invalid.

Author's conduct (only one response allowed):
☐ honest error
☐ academic misconduct
X none (not applicable in this case – e.g. in case of editorial reasons)

*   Also called duplicate or repetitive publication. Definition: "Publishing or attempting to publish substantially the same
    work more than once."

History
Expression of Concern:
☐ yes, date: `yyyy-mm-dd`
X no

Correction:
☐ yes, date: `yyyy-mm-dd`
X no

Comment:

This article has been retracted to straighten the academic record. In making this decision the Editorial Board follows COPE's Retraction Guidelines. Aim is to promote the circulation of scientific research by offering an ideal research publication platform with due consideration of internationally accepted standards on publication ethics. The Editorial Board would like to extend its sincere apologies for any inconvenience this retraction may have caused.

Scientific
Research

Efficiency of Amphoteric Surfactants as Flow Improvers and Pour Point Depressants

Noura El Mehbad

Faculty of Science, Nagran University, Saudi Arabia of Kingdom.
Email: dr.n.almehbad@hotmail.com

ABSTRACT

Some amphoteric surfactants (N-Decyl-N-benzyl-N-methylglycine(AB) and N-Dodecyl-N-benzyl-N-methylglycine(CD) were prepared in the laboratory. The physicochemical chemical 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 that 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. The mechanism of the depressants action has been suggested according the adsorption of each additive. 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.

Keywords: Wax; Additives; Pour Point; Amphotric Surfactants; Waxy Gas Oil

1. Introduction

In our previous work the synthesis of new additives as pour point and antioxidants was described [1-3]. Pour point of petroleum products, basically heavy fuel and lubricating oils, are defined as the lowest temperature at which the petroleum product is observed to flow when cooled and below this temperature the product is stopped to flow. Polyalkylphenol formaldehyde sulphonate and its ethoxylate were synthesized and evaluated as pour point depressant, viscosity improver and antioxidant. The efficiency of these additives depends on their chemical structure and degree of mixing (mole fraction). Values of surface tension of these additives were measured in oil phase and consequently CMC was determined for all additives and their mixtures. A novel method of inhibiting oxidation was proposed. The author suggests the mechanism according to surface activity of additive in oil phase. More confirmations for suggested mechanism were investigated by measuring the area occupied per molecule of additive at oil phase. The results indicate that the compatibility of sulphonate with ethoxylate group and forming stable micelle which act as wax dispersant and improver viscosity [1]. Some anionic surfactants had been applied as pour point depressant by Omar *et al.* [4].

It is found that, the surface parameters and free energies of micellization and adsorption confirm the decreasing and improving of pour point. Also it is found that there is a good relation between surface properties especially interfacial tension of the surfactants and their efficiency in depressing the pour point. Cacium octadecyl benzene sulphonate and octadecyl phenol ethoxylate with 6 units of ethylene oxide were synthesized and evaluated as pour, cloud points depressants and viscosity index improvers. These additives were compared with imported natural wax dispersing agent. It is found that increasing concentration of these additives is accompanied by an increase in the minimum area occupied per molecule and surface excess concentration. There is a good relationship between the structure of hydrophilic group of the additive and its efficiency.

Mixing the binary additives enhances its efficiency [5]. On the other hand the physical properties of the mixed system of cationic/nonionic surfactant and its efficiency in pour point depression were studied elsewhere [6]. 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. Some ester is widely used as lubricants and high performance industri-

al fluids. They are characterized by good biodegradability, low volatility, good lubricity, good thermal stability and low pour points. Action mechanism of sorbitan palmitate as multifunction additive for pour, cloud points depressant and viscosity improver with oxidation of oil. The efficiency of this additive depends on its critical micelle concentration. The micelle core act as trap for hydrocarbon oxide radicals and terminate chain of hydrocarbon oxidation. The micellar inhibition depend on incorporation of hydroperoxide or other polar oxygen containing molecules to the reversed micelle, as the results increase oxidation stability of oil [3]. The author studies new antioxidant for lube oil. This antioxidant dibenzyl s-phenyl thio glyconitrile and other derivatives were prepared phase transfere catalysts. These compounds were added to oil in different concentrations. The antioxidants activities of different dosages were evaluated and suggested mechanism according to micelle and their thermodynamic [1].

The purpose of the present work study of prepared amphoteric surfactants calcium salt of N-Decyl-N-benzyl-N-methylglycine (AB) and N-Dodecyl-N-benzyl-N-methylglycine (CD) which differs in hydrocarbon chain length and apply as pour point and anti oxidant for the paraffinic gas oil.

2. Experimental

Preparation the additive by phase transfer catalysts by two techniques:

N-Decyl-N-benzyl-N-methylglycine(AB) and N-Dodecyl-N-benzyl-N-methylglycine(CD) were synthesized by Omar [7]. 3 mol N methyl benzylamine and 1 mol calcium chloroacetate to react overnight in pure ethanol at 50 C^0 in the presence of 0.1 mol of benzyl triethanol ammonium chloride as phase transfere catalyst. The resulting solution was treated with sodium carbonate and recrystallized by alcohol. The resulting prolcoduct calcium salt of N-Decyl-N-benzyl-N-methylglycine (AB) and N-Dodecyl-N-benzyl-N-methylglycine (CD).

Surface tension of different concentrations for 10^{-7} to 0.1 mol/L of the synthesized additives were measured by using Kruss Model 8451 in petroleum ether at 30°C according to omar *et al.* [8].

The oxidation test was carried out at 120°C 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. The investigated amphoteric surfactant was added in different concentrations. Pour point depressants and viscosity according to ASTM-D 97 and IP 71/80 respectively.

3. Results and Discussions

Detailed physic-chemical characteristics of the paraffinic

oil are reported in **Table 1**. The prepared compounds were confirmed their chemical structure by micro elemental analysis and IR spectra. These compounds can only exist in two forms, either amphoteric ions or cationics ions. The IR spectra of the synthesized compound showed the following bands: Absorption band at 1590 - 1330 cm^{-1} characterized the carboxylate group. The C-N streching vibration band is at 1590 cm^{-1}, while strong absorption bands at 1540, 1670 cm^{-1} were found to streching vibrations of carbonylgroup (**Figure 1**). The variation of surface tension with concentration is shown in **Figures 2** and **3**. 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 (hydrocarbon group). The action of additive of oil phase can be calculated using Gibbs adsorption equation [7,8]. Comparing the data in **Table 2** shows that the CMC value for the compound (CD) was lower than that of the compound (AB), which indicates that the former CD favors micellization processes at a lower concentration than the latter compound. Studying the results in **Table 2**, shows that the synthesized amphotric surfactants CD have large values of surface excess and minimum surface area, indicating the CD is the most efficient and gives a greater lowering in surface tension of oil. Thus the change in hydrocarbon group of (hydrophobic part) affect of degree of micellization which will be reflected of efficiency of the additive of its activity in oil phase. This concept is clearly observed in **Figure 2**. From this figure, as concentration increases, the surface excess concentration increase to reach a constant value at CMC, while the additive CD has large value than AB as shown in **Table 2**. These results confirm the compound CD more solublize and more active in oil phase. These results are compatible by the author [1-3]. 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* [7,8] as shown in **Table 3**. ΔG_{mic}

Table 1. The physicochemical properties of the base oil.

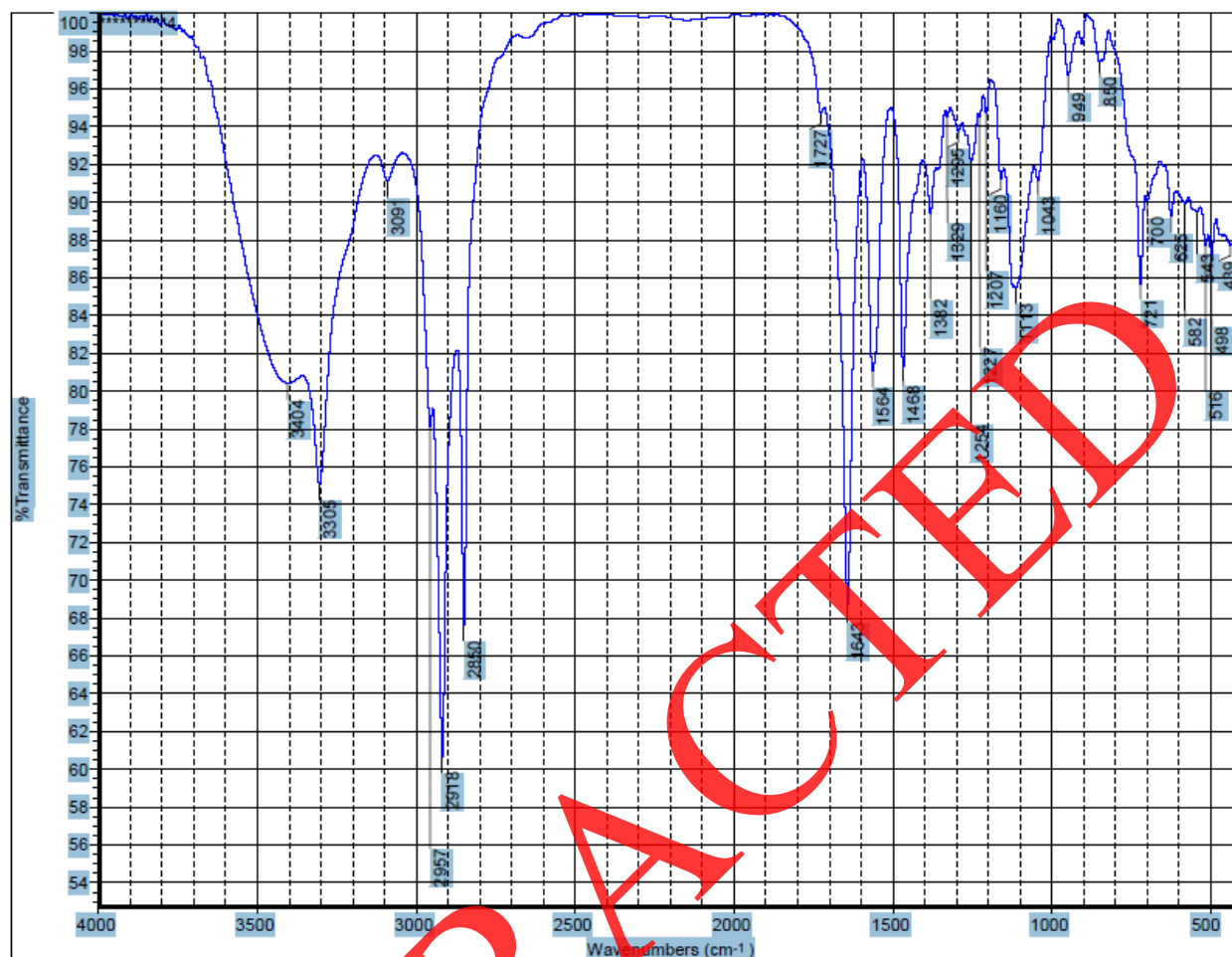| Properties	Base oil	Test
Denisty (g/ml) at 15.5°C	0.8958	D. 1298
Refactive index nD^{20}	1.4955	D. 1218
ASTM colour	4.5	D. 1500
Kinematic viscoslty cSt		
at 40°C	17.56	D. 445
at 100°C	29.15	D. 455
Pour point C	15	ASTM D 97
Molecular weight	520	GPC
Total paraffinic content, wr%	59.353	Urea adduction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

Figure 1. I.R spectra of CD additive.
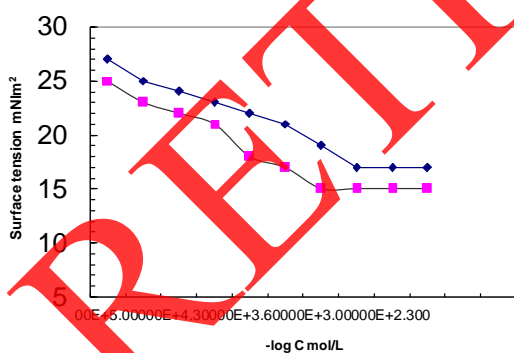
Figure 2. Effect of additive concentration on surface tension reduction of oil at different temperature for the additive AB.

Figure 3. Effect of additive concentration on surface tension reduction of oil at for the additive CB different temperature.

values are negative indicating that the processes of micellization processes is a spontaneousity depend mainly on the hydrocarbon chain length, while ΔS_{mic} are 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 is increased by increasing the temperature.
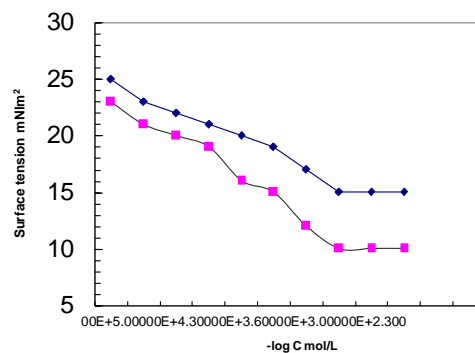
On the other hand ΔH_{mic} values are positive due to the endothermic process of amphoteric solvation upon micellization.

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

Table 2. Surface properties of additives at different temperatures.

Compound	T, ˚C	-log (CMC)	$A_{min} \times 10^2$ nm^2	$\Gamma_{max} \times 10^3$ mol/cm^2	Critical surface tension Mn/M^2
AB	20	2.25	45.5	5.7	17
	30	2.27	43.5	4.6	15
CB	20	3.01	95	2.5	14
	30	2.29	160	0.86	12

Table 3. Thermodynamic parameters of additives at different temperatures.

Compound	T, ˚C	ΔG_{mic} KJ/MOL	ΔS_{mic} KJ/MOL	ΔH_{mic} KJ/MOL	ΔG_{ads} KJ/MOL	ΔS_{ads} KJ/MOL	ΔH_{ads} KJ/MOL
AB	20	−12.45			−13.55		
	30	−13.1	0.06	4.9	−14.76	0.02	6.8
CB	20	−15.8			−16.9		
	30	−18.5	0.07	−9.72	−19.8	0.01	9.2

Table 4. Effect of different additives on pour point at different concentrations.

Adittive	Conc mollL	Pour point, C	Kinematics viscosity, cSt at different temperatures	
			40 C	100 C
AC	0.000002	13	17	26.14
	0.0000025	10	10	15
	0.000003	7	8	10
	0.0000035	5	7	5.1
	0.000004	4	7	5.5
CB	0.000002	10	18	20
	0.0000025	7	13.7	17
	0.000003	4	12.5	7
	0.0000035	2	13	6
	0.000004	2.5	12.5	7

responding to the micellization processes. This indicates that the adsorption processes of surfactant molecules is more energetically favored and these molecules act as free before micellization. The results the activity of these surfactants reach maximum at CMC and tend to steady stable until limit value and scissors or decay. This value has the critical surface tension and interfacial tension. Furthermore, the higher positive values standard of free standard entropy change, ΔS_{mic}, and standard enthalpy change, ΔH_{mic} confirm the above mention and molecules of surfactants prefer the adsorption at the interface rather than formation micelle. At higher temperature, increase the negativity of standard free energy, ΔG_{mic} and the positivity of standard entropy ΔS_{mic}, which confirmed the adsorption preferability of the amphoteric surfactants at oil interface at higher temperatures. So below CMC the surface tension represents the critical value for adsorption and it's activity of free molecules of surfactants (**Table 3**).

It can be concluded that, the activity of the additive in oil phase enhances by degree of temperature and the values of CMC. This is due to the fact the moiety of molecules increases, as results increase their adsorption rather than giving stable micelle. These results are depicted on **Table 3**.

The investigation of the ability of additives as pour point depressant and viscosity improver are shown in **Tables 4**. It is clear that the pour point and kinematic viscosity are improved by increasing the additive concentration. The optimum value for reduction pour and kinematic viscosity at its the critical micelle concentration. These results can be discussed according the surface properties of the additive and its thermodynamic parameters (**Tables 2** and **3**). From the structure of additive, it has lyophilic part like the paraffinic wax which completely miscible with wax molecule, while the lyophobic group (COO^-, or N^+ group) adsorbs at interface. The author suggests the conversion of the amphoteric species to the protonated cationic form which is characterized by less surface activity. *i.e* the free molecules can act as cationic or ioic surfactants depend on the hydrogen proton in oil phase. As the results, disperse wax crystal lattice to small sizes, consequently the pour point decreases and viscosity improves. *i.e* these addictives have multifunction purposes.

The effect of these addictives on the oxidation stability of oil is given in **Figure 4**. The data shows the additive retards the oxidation of oil COO^- group and CN^+ in each additive, which act as trap for free radical of R-O. From **Figure 4**, the total acid decrease by increasing the addi-
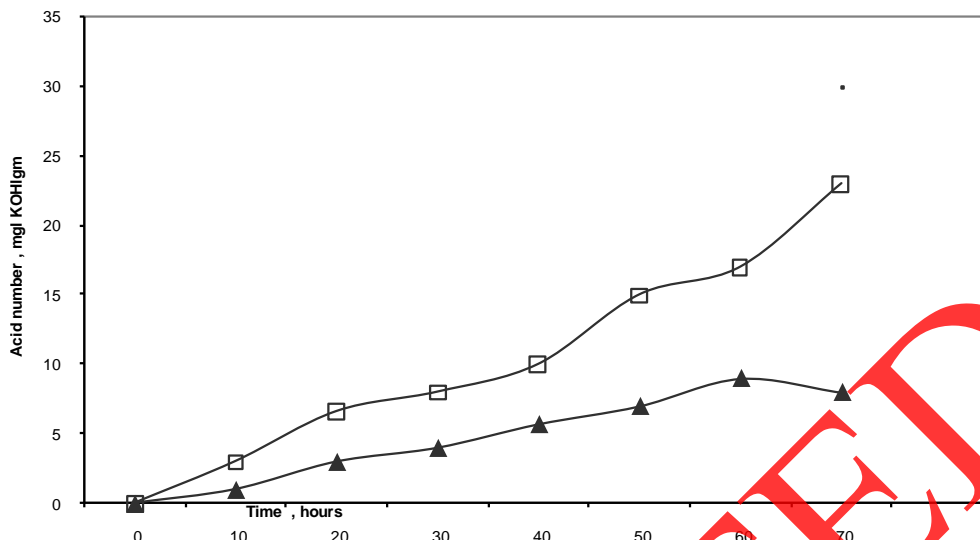
Figure 4. Effect of different concentrations of the prepared additive son acid number.

tive concentrations and reach the optimum value at CMC each additive as confirmed by the author early [1-3]. Further increase concentration of the additive, the oxidation stability decreases due the increase in surface tension, which affects on interfacial tension and degree of adsorption at interface. Comparing between two additives in increasing oil stability, the additive CD is the slightly high of AB, due to it has the surface properties slightly small difference. The COO^- group inhibits propagation of free radicals and terminates reaction processes of free radicals.

4. Conclusion

1) The oxidation stability of oil as measured by total acid number indicates that, the oxidation inhibitor efficiency follows the order.

CD > AB. These results depend on value of CMC and area occupied per molecule at oil interface and thermodynamic parameters of surfactants.

2) The synthesized additives have a multifunction for pour point depressant, improving viscosity and enhance oxidation stability of oil. These results depend on adsorption of additives at oil phase and critical surface tension.

REFERENCES

[1]   N. El Mehbad, "Development Antioxidants Synthesized by Phase Transfer Catalysts for Lubricating Oil," *Biotech Conference*, Expo, 12-16 May 2013.

[2]   N. El Mehbad, "Developments of Multifunctional Additives for High Quality Lube Oil," *Journal of Power and Energy Engineering*, Sanya, 29 November - 1 December 2013.

[3]   N. El Mehbad, "The Development and Application of Ester for Lubricating Oil by Phase Transfer Catalysts," *19th International Colloquium*, 21-23 January 2013, Germany.

[4]   T. T. Khidr, E. M. S. Azzam, S. Mutwaa and A. M. A. Omar, "Study of Some Anionic Surfactants as Pour Point Depressant Additives for Wax Gas Oil," *Industrial Lubrication and Tribology*, Vol. 59, No. 2, 2007, pp. 64-68. http://dx.doi.org/10.1108/00368790710731855

[5]   T. T. Khidr and A. M. A. Omar, "Anionic/Nonionic Mixture of Surfactants for Pour Point Depression of Gas Oil Egyptian," *Journal of Petroleum*, Vol. 12, 2003, pp. 21-26.

[6]   T. T. Khidr, D. Ismail and A. M. A. Omar, "Improving the Flow Properties of n-Paraffin Gas Oil by Cationic and Non-Ionic Surfactants," *Journal of Faculty of Education*, Vol. 25, 2000, pp. 121-135.

[7]   A. M. A. Omar, "Separation of Emulsifiable Oil from Solution by Surface Tension Control," *Adsorption Science and Technology*, Vol. 19, No. 1, 2001, pp. 91-100. http://dx.doi.org/10.1260/0263617011494006

[8]   A. M. A. Omar, *Journal of Petroleum Science and Technology*, Vol. 19, No. 7-8, 2001, pp. 11-21.