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Some Cutting Oil Formulations Based on Local Prepared Emulsifiers Part I: Preparation of Some Emulsifiers Based on Local Raw Materials to Stabilize Cutting Oil Emulsions

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The first main target of this work is to synthesis some emulsifiers from local raw materials used for cutting oil formulations. Seventeen emulsifiers (15 nonionic and 2 anionic) were prepared from locally available materials such as linear alkyl benzene sulfonic acid (LABSA), glycerol, polyethylene glycol, and maleic anhydride. Their chemical structures were confirmed using FTIR. The surface tension for the emulsifiers was measured at 25°C, and the surface and thermodynamic properties were calculated based on the surface tension parameters. The formulations of cutting oil fluids were prepared using these emulsifiers. The second target is to investigate the stability of soluble oil blends and emulsion stability of soluble oil in water. The results are discussed in the light of surface-active properties and chemical structure of emulsifiers.

Keywords Cutting fluids, emulsifiers, soluble oils, emulsion stability, coupling agents, cutting oil emulsions

INTRODUCTION

Cutting fluids are used for a number of objectives: to prevent the tool, workpiece, and machine from overheating, improve surface finish, and help clear swarf from the cutting area (Trent, 1984; Pandazaras et al., 2001; Chen et al., 2001). Basically, there are two major groups of cutting fluids, water-based or emulsifier oils (soluble oil) and neat cutting oils (Shoji et al., 1982). The soluble mineral oils are the most widely used for metal working operations because they offer the following advantages: (1) reduction of heat, allowing higher cutting speeds, (2) cleaner conditions, (3) more economical dilution with water, bringing down application costs, (4) better operator acceptance (cooler, cleaner parts), and (5) improved health and safety benefits: no fire hazard and reduction of oil misting and fogging.

Emulsifiable cutting fluids consist of an emulsion, usually a mineral oil in water in a 1:5 to 1:50 oil-to-water ratio. The science of formulating soluble oils has progressed from soluble oils that are unstable after a few working cycles, through the cooling systems in the 1930s, to soluble oils that are stable for many cycles in machine recirculation systems

today. Emulsifiable oils (soluble oils) form milky emulsions when mixed with water. The most important characteristic of a soluble oil is that it emulsify easily to form stable emulsions. Soluble oils have rather complex compositions, usually containing two or more emulsifiers, coupling and stabilizing agents, and additives to provide rust inhibition, lubricity, detergency, and resistance to bacterial attack. The relative concentrations of components are delicately balanced to ensure that the finished compositions will remain stable until used (Kipers et al., 1983; Barkat et al., 1998). In many cases a package emulsifier system is put together, which contains nonionic emulsifiers, soap, oil-soluble sulphonates, and coupling agents (O'Connor, 1968; Men et al., 2001; Diatto, 2002). Cutting fluids are manufactured from high-quality base oils and blended with additives to give the desired properties of cooling, lubricity, extreme pressure resistance, and rust inhibition. As a result, the proper selection of a cutting fluid involves assessment of a combination of operational and fluid property factors and should be made by knowledgeable personnel (Carver, 1984; Axinte et al., 2001). Commercial emulsifier packages are expensive, so the main object of this work is to prepare some emulsifiers based on local raw materials used for cutting oil formulations. Our attention extended to measure surface tension and calculate some

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surface-active properties of some emulsifier solutions and their emulsion formulations to learn the role of surface tension in stabilization of cutting oil fluids.

EXPERIMENTAL

The chemicals used in this work were obtained from different Egyptian local companies and all were of technical and analytical grade.

Synthesis of Nonionic Emulsifiers Based on LABSA

One mol of linear alkyl benzene sulfonic acid (LABSA) was heated for 4 h at 170°C in the presence of 2% ZnO (continuous stirring) with monoethanol amine (MEA), diethanol amine (DEA), polyethylene glycol 400 (PEG), and tetraglycerol individually to produce products Ia, Ib, Ic, and Id respectively. Products Ia and Ib were further heated with one mole glycol in the presence of 2% of zinc oxide to produce Ia₁ and Ib₁ respectively (Jonsson, 1931). Table 1 shows the chemical structure, name, and designation of these derivatives.

Synthesis of Nonionic Emulsifiers Based on Maleic Anhydride Esters and Adduct with Oleic Acid

In a three-necked flask connected by a Dean-Stark sidearm, 0.1 mol of cetyl or octadecyl alcohol and 0.1 mol of polyethylene glycol, M. wts 400, 600, or 1000, was mixed individually. The mixture was heated in the presence of 100 mL xylene and 2% zinc oxide up to reflux temperature (140°C). Then 0.1 mol of maleic anhydride (MA) was added gradually with continuous stirring for 4 h until the theoretical amount of water was collected. Table 2 shows the chemical structure, name, and designation of the maleic anhydride derivative emulsifiers.

One mole of maleic anhydride was added to one mol of oleic acid in a one-necked flask with condenser. The mixture was heated to 190°C for 4 h to form oleic maleic anhydride adduct (OM). Then 0.5 mol of OM adduct was charged in a three-necked flask joined with a Dean-Stark sidearm. The 0.5 mol PEG400, 0.5 mol PEG600, 0.25 mol PEG400 + 0.25 mol octadecyl alcohol, or 0.25 mol PEG600 + 0.25 mol cetyl alcohol was added in the presence of p-toluene sulfonic acid and 200 mL xylene until the theoretical amount of water was collected at reflux temperature 140°C (Chales, 1947). The chemical structure, name, and designation of the oleic maleic anhydride adduct emulsifiers are shown in Table 3.

Synthesis of Nonionic Emulsifiers Based on Ester and Ethylene Oxide

To prepare ethoxylated (20) sorbitol trioleat, 1 mol of sorbitol and 3 mol of oleic acid were mixed in a three-necked flask joined with a Dean-Stark sidearm and condenser, then the mixture was heated at 140°C in the presence of xylene and 2% ZnO for 4 h to give sorbitol trioleate. The ethoxylation of sorbitol trioleate was carried out by injection of ethylene

oxide gas to the reaction vessel (autoclave), under nitrogen atmosphere and 0.1% sodium metal as a catalyst. The reactants were heated up to 170 to 180°C for 4 h at different time intervals, after which the apparatus was filled with nitrogen, then cooled and the reaction vessel was weighed. The difference in weight indicated the amount of consumed ethylene oxide (Lang et al., 1999). The prepared compound was ethoxylated (20) sorbitol trioleate (E(20)STO).

Purification of Nonionic Emulsifier

The product was dissolved in isopropanol (v/v), mixed with an equal volume of oversaturated sodium chloride solution (salting out), and allowed to stand at 90°C with continuous stirring for one hour. The produced lower layer was drawn off and discarded; the upper layer is the nonionic emulsifier dissolved in isopropanol, which was distilled off to obtain the pure product (Schwartz, 1952).

Synthesis of Anionic Emulsifier Based on LABSA

One mol of alkyl benzene sulfonic acid was heated with 1 mol of diethanol amine in ethanol for 4 h at reflux temperature (78.5°C) with continuous stirring. The product was precipitated and the solvent was discarded to obtain diethanol ammonium alkyl benzene sulfonate (DAABS) (Renault, 1972; Al-Sabagh et al., 2004).

To prepare sodium alkyl benzene sulfonate, the alkyl benzene sulfonic acid was neutralized by 10% sodium hydroxide solution with stirring and heating on a water bath until the mixture become slightly alkaline using phenolphthaline indicator. The product was then recrystallized in absolute ethanol. The ethanol was decanted to give pure sodium alkyl benzene sulfonate (SABS) (Renault, 1972; Al-Sabagh et al., 2004).

Surface Tension Measurements


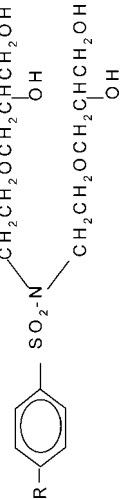
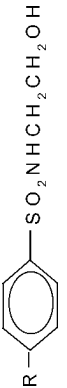


These measurements were made using the Dagnon Abribat tensiometer. The instrument was calibrated by double-distilled water each time that a new measurement was made. The measurements were taken at 25°C.

EVALUATION OF EMULSIFIER SYSTEMS AS METAL WORKING FLUIDS (SOLUBLE OILS)

Preparation of Soluble Oil Blends

The formulation of soluble cutting oil blends was made in two steps: the first step is to formulate the cutting oil emulsifier package and the second step is to blend the emulsifier package with base oil to form the final soluble cutting oil formula. The emulsifier package contains primary emulsifier, secondary emulsifier, fatty acid, amine, and coupling agent (Eckard et al., 1991). The emulsifier packages prepared were composed of many variables including:

TABLE 1
Chemical structure, IUPAC name, and abbreviation of emulsifiers based on LABSA

Chemical structure of emulsifiers	IUPAC name	Abbreviation	Code in Scheme 1	Molecular weight	HLB ^a
	Alkyl benzene-N-glycerol sulfonamide	ABEGSA	Ia ₁	443	8.939
	Alkyl benzene-N-diethoxyglycerol sulfonamide	ABDEGSA	Ib ₁	561	11.265
	Alkyl benzene-N-ethoxy sulfonamide	ABESA	Ia	369	6.720
	Alkyl benzene-ethoxylate(9) sulfone	ABE(9)S	Ic	725	13.240
	Alkyl benzene-polyglycerol(4) sulfonate	ABPG(4)S	Id	622	12.122

^aHydrophilic-lipophilic balance (HLB = $M_H/M_H + M_L \times 20$), where M_H is the M. wt of hydrophile and M_L is the M. wt of lipophile.

TABLE 2
Chemical structure, IUPAC name, and abbreviation of emulsifiers based on maleic anhydride esters

Chemical structure of emulsifiers	IUPAC name	Abbreviation	Code in Scheme 2	Molecular weight	HLB
$\text{C}_{16}\text{H}_{33}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{HC}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_9-\text{H}$	Ethoxyl(9)cetyl-maleate ester	E(9)CME	IIa1-1	739	12.016
$\text{C}_{16}\text{H}_{33}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_{13-6}-\text{H}$	Ethoxyl(13.6)cetyl-maleate ester	E(13.6)CME	IIa1-2	939	15.594
$\text{C}_{16}\text{H}_{33}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_{22-7}-\text{H}$	Ethoxyl(22.7)cetyl-maleate ester	E(22.7)CME	IIa1-3	1339	15.594
$\text{C}_{18}\text{H}_{37}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{HC}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_9-\text{H}$	Ethoxyl(9)octa-decyl-maleate ester	E(9)ODME	IIa2-1	767	11.577
$\text{C}_{18}\text{H}_{37}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{HC}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_{13-6}-\text{H}$	Ethoxyl(13.6)octa-decyl-maleate ester	E(13.6)ODME	IIa2-2	967	13.32

TABLE 3
Chemical structure, IUPAC name, and abbreviation of emulsifiers based on oleic maleic anhydride adduct

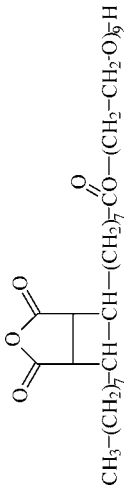
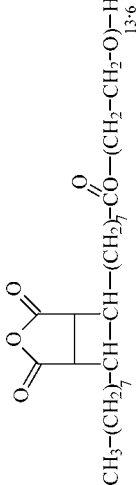
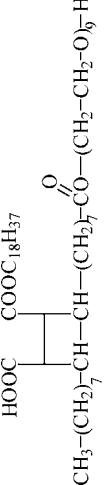
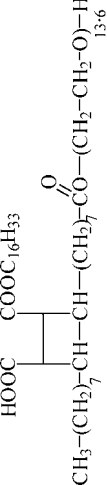
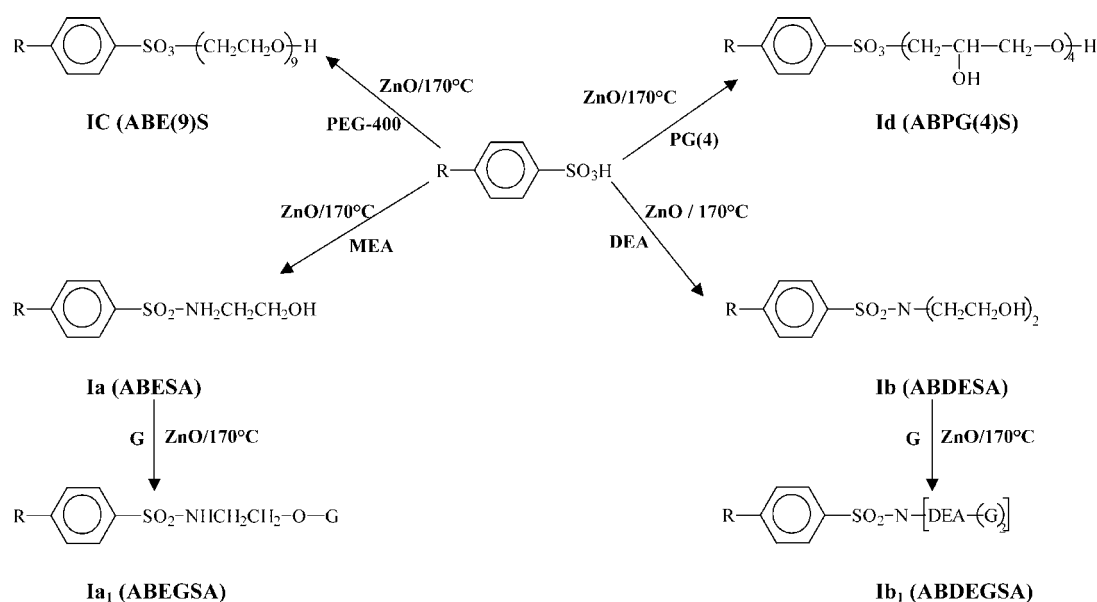
Chemical structure of emulsifiers	IUPAC name	Abbreviation	Code in Scheme 3	Molecular weight	HLB
	Ethoxyl(9)maleic-anhydride oleic acid adduct	E(9)OM	IIb1	779	11.399
	Ethoxyl(13.6) maleic-anhydride oleic acid adduct	E(13.6)OM	IIb2	979	13.156
	Ethoxyl(9) octa decyl-oleic acid maleate adduct	E(9)ODOM	IIb3	1049	8.465
	Ethoxyl(13.6) cetyl-oleic acid-maleate adduct	E(13.6)COM	IIb4	1221	10.548

TABLE 4
The trial range of formulated emulsifier packages of soluble cutting oil, using different variables

Emulsifier package components	Percentage of each component in cutting oil formula	
	Trial range, %	Optimum range, %
1. Emulsifier	0.4–4.0	1.8–3.4
2. Oleic acid	3.0–12.0	11.5–12.0
3. Diethanol amine	1.0–4.5	3.0
4. Coupling agents		
a. Cyclohexanone	0.0–10.0	2.0
b. Petroleum spirit	0.0–10.0	2.0
c. Amyl alcohol	0.0–10.0	4.0–5.0

TABLE 5
The physical and chemical properties of local base oil (140/160)

Test	Method	Result
1. Kinematic viscosity at 40°C C.St	ASTM 445	30
2. Kinematic viscosity at 100°C C.St	ASTM 445	5
3. Viscosity index	From tables	95
4. Flash point closed, °C	ASTM 93	170
5. Pour point, °C	ASTM 96	–5
6. Color	ASTM 1500	2.5
7. Total acid number (mg KOH/g)	ASTM 664	0.05
8. Percentage of aromatic compound (CA%)	Column chromatography	13
9. Ratio of paraffinic compound (CP%)	Column chromatography	63
10. Ratio of naphthenic compound (CN%)	Column chromatography	24



SCH. 1. Preparation of nonionic emulsifiers based on LABSA; G, glycerol; DEA, diethanol amine; MEA, monoethanol amine; PG(4), polyglycerol 4; PEG, polyethylene glycol 400.

1. Variation of emulsifiers to examine them individually at various concentrations until the best concentration at which the emulsion stability of soluble oil blends in water was obtained.
2. Fatty acid (oleic acid) was used in this investigation.
3. Alkanol amine (diethanol amine) was used.
4. Coupling agent: three coupling agents, cyclohexanone, amyl alcohol, and petroleum spirit (organic solvent), were examined. The trial range to formulate the emulsifier packages using these variable components is shown in Table 4.
5. Diluent oil: local base oil was used in the formulation processes for soluble oils; the chemical and physical properties are shown in Table 5.

Stability of Soluble Oil (Screening Test)

According to the standard test method (IP 311), the soluble oil was prepared by adding the proposed components to a sample bottle. All bottles were capped and placed in the oven at 50°C for a period of not less than 15 h and not more than 20 h. At the end of this period, the oil was examined immediately for any indication of turbidity, separation, or gelling, and the blend that gave a stable soluble oil (no gel formation, no separation) was selected for further investigation.

Emulsion Stability Test

The standard test method (IP 263) for emulsion stability was carried out for all blend samples that gave the more stable soluble oil. Emulsion stability was tested on 5 and 10% solutions of soluble oil in distilled water, which contains 0.688 g/L of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to give hardness of 400 ppm in terms of CaCO_3 . In this test, the emulsion was prepared at 5 or 10% soluble oil percentages as follows:

1. 152 or 135 mL of the prepared hard water in a 250 mL conical flask was stirred using a magnetic stirrer.
2. 8 or 15 mL of the formulated soluble oil was added quickly with continuous stirring for 2 min, then the prepared emulsifier was poured in a measuring graduated flask. This flask was left for 24 h to check emulsion stability (separation, gelation, or completely stable). Only soluble oils that exhibited remarkable emulsion stability (0.5% vol cream or less and no oil layer separation after 24 h) should pass at this evaluation.

RESULTS AND DISCUSSION

Metal working fluids are formulated to provide cooling, lubrication, and rust protection at cutting, processing, and machining of metals. Basically, there are two types of metal working oils: soluble and neat oil. Mineral oils containing one emulsifier system to make them soluble in water, called "soluble oils," are used as coolant. These materials can be diluted with water to form stable emulsions over a wide

range of concentrations. These emulsifiers break the oils into minute particles and keep the particles, dispersed in water for long periods of time. In this work, the first target is to synthesize some emulsifiers from local raw materials, and the second target is to formulate an efficient metal working emulsion. The considered emulsifiers have been prepared from locally available materials such as linear alkyl benzene sulfonic acid, glycerol, polyethylene glycol, and maleic anhydride.

Five nonionic emulsifiers based on LABSA (ABE GSA, ABDE GSA, ABESA, ABE(9)S, and ABPG(4)S) and also two anionic emulsifiers (DAABS, SABS) were prepared according to the methods in the above experimental part. The equations of reactions are shown in Scheme 1. The emulsifier (LABDE GSA) was used to confirm the chemical structure using Fourier transform infrared spectroscopy (FTIR). As shown in the spectra of Figure 1(a),

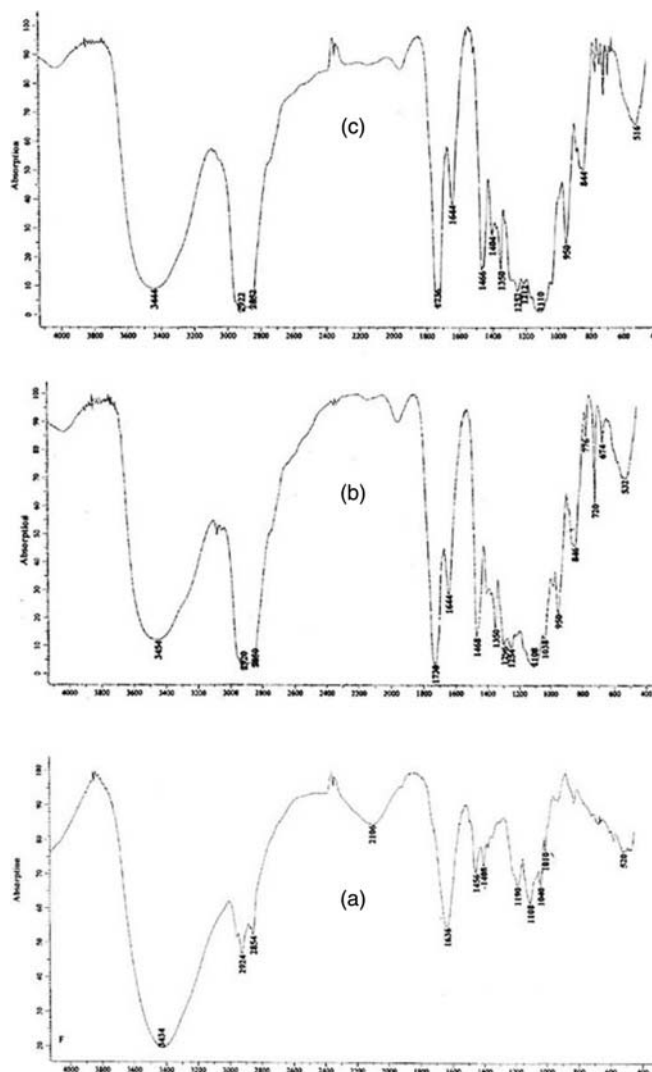
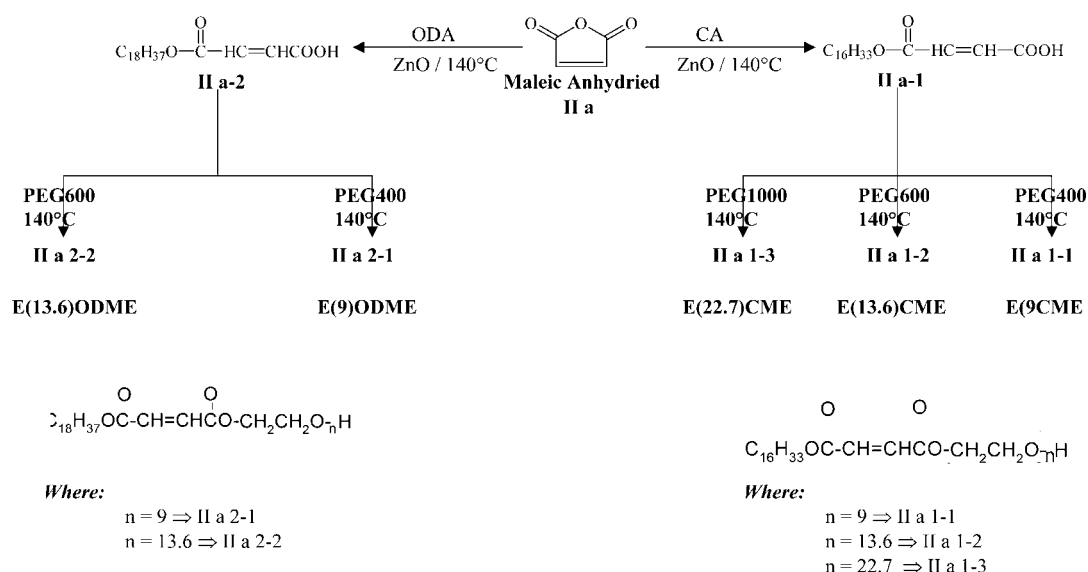


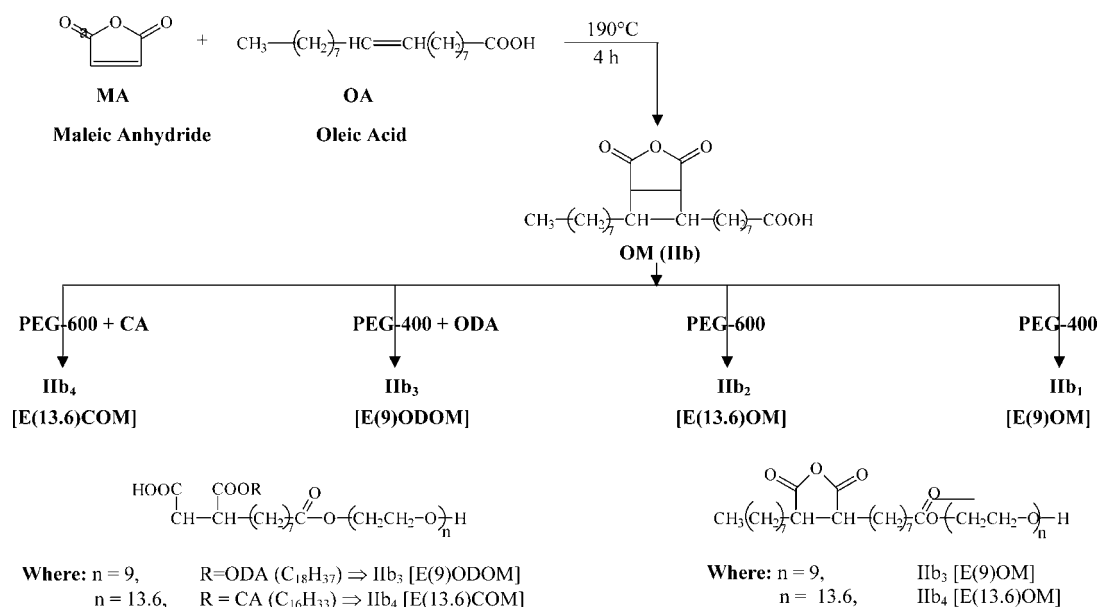
FIG. 1. FTIR spectra of (a) ABDEGSA, (b) E(9)CME, (c) E(9)ODME.



SCH. 2. Preparation of nonionic emulsifiers based on maleic anhydride ester; CA, cetyl alcohol; ODA, octadecyl alcohol; PEG, polyethylene glycol.

the sharp stretching band at 3434 cm^{-1} pointed to alcoholic (OH). The stretching band at 1408 cm^{-1} pointed to the presence of (C-SO₂-N), while the stretching band at 1190 cm^{-1} corresponds to (S=O). Also, the stretching band at 1108 cm^{-1} pointed to the presence of etherial bond (C-O-C), and the stretching band at 1636 cm^{-1} pointed to (C=C aromatic ring). Five nonionic emulsifiers based on maleic anhydride ester were prepared according to the methods in the above experimental part. The equations of reaction are shown in Scheme 2. The FTIR of E(9)CME

was used to confirm the chemical structure of this group; as shown in Figure 1(b), the sharp stretching band at 3454 cm^{-1} pointed to alcoholic (OH). The stretching band at 1730 cm^{-1} pointed to the presence of ester group (COO-), while the stretching band at 1644 cm^{-1} pointed to the unsaturated double bond (HC=CH). Four nonionic emulsifiers based on oleic maleic anhydride adduct were prepared according to the method in the experimental part. The equations of reaction are shown in Scheme 3. The FTIR of E(9)ODME was used to confirm the chemical structure of



SCH. 3. Preparation of nonionic emulsifiers based on oleic maleic anhydride adduct; OA, oleic acid; MA, malic anhydride; CA, cetyl alcohol; ODA, octadecyl alcohol; PEG, polyethylene glycol.

TABLE 6
Surface-active and thermodynamic properties of prepared emulsifiers

Emulsifier	M. wt	γ_{CMC} , mN m^{-1}	CMC, mol/dm^3	π_{CMC} , mN m^{-1}	$\Gamma_{\text{max}} \times 10^{10}$ mol/cm^2	A_{min} , nm^2	ΔG_{mic} , kJ mol^{-1}	ΔG_{ad} , kJ mol^{-1}	Successful formulation no.
ABEGSA	443	29.8	28.21×10^{-5}	42.59	26.2	63.37	-20.25	-21.87	1
ABESA	369	30.2	33.87×10^{-5}	42.19	30.3	66.40	-19.8	-21.48	2
ABDEGSA	561	29.9	22.28×10^{-5}	43.79	25.8	64.35	-20.83	-22.23	3
ABPG(4)S	622	27.4	20.09×10^{-5}	44.99	30.3	66.40	-21.09	-22.89	4
ABE(9)S	725	27.0	17.024×10^{-5}	45.39	25.5	66.40	-21.47	-23.28	5
DAABS	431	34.4	29×10^{-5}	37.99	30.3	54.79	-20.18	-21.43	6
SABS	348	35.0	35.9×10^{-5}	37.99	30.3	54.79	-19.65	-20.88	7
E(9)CME	739	31.9	16.91×10^{-5}	40.69	25.0	54.79	-21.52	-22.86	8
E(13.6)CME	939	32.4	13.31×10^{-5}	39.99	30.3	54.79	-22.11	-23.43	9
E(22.7)CME	1339	26.8	9.33×10^{-5}	45.59	30.3	54.79	-22.99	-24.49	10
E(9)ODME	767	30.0	16.29×10^{-5}	42.39	25.0	54.79	-21.16	-23.01	11
E(13.6)ODME	967	27.4	12.92×10^{-5}	44.99	30.3	54.79	-22.18	-23.66	12
E(9)OM	779	30.2	16.04×10^{-5}	42.19	30.3	54.79	-21.65	-23.04	13
E(13.6)OM	980	34.8	12.75×10^{-5}	37.59	30.3	54.79	-22.22	-23.46	14
E(9)ODOM	1049	34.8	11.9×10^{-5}	37.59	30.3	54.79	-22.39	-23.63	15
E(13.6)COM	1221	28.6	10.23×10^{-5}	43.79	30.3	54.79	-22.76	-24.21	16
E(20)STO	1841	29.2	6.78×10^{-5}	43.19	30.3	54.79	-32.78	-25.20	17

TABLE 7
Effect of surface tension on emulsion stability of some prepared formulations of cutting oil

Formulation of cutting oil	ABPG(4)S			ABE(9)S			E(22.7)CME			E(13.6)ODME			E(13.6)COM			E(20)STO + amyl alcohol	
	18	4		21	4		11	10	6	12	7	16	1	17			
Ingredient																	
Emulsifier % wt	2.4	2.4		2.4	2.4		1.8	1.8	2.2	2.2	1.8	1.8	19.0	15.5			
Oleic acid % wt	11.7	11.7		11.7	11.7		10.0	11.7	10.0	11.7	10.5	11.5	—	—			
Diethanol amine % wt	1.5	3.0		4.0	3.0		3.0	3.0	3.0	3.0	3.0	3.0	—	—			
Amyl alcohol % wt	5.0	5.0		5.0	5.0		5.0	5.0	5.0	5.0	5.0	5.0	1.0	4.5			
Petroleum spirit % wt	2.0	2.0		2.0	2.0		2.0	2.0	2.0	2.0	2.0	2.0	—	—			
Cyclohexanone % wt	2.0	2.0		2.0	2.0		2.0	2.0	2.0	2.0	2.0	2.0	—	—			
Test																	
Surface tension (mN m ⁻¹)	36.9	27.8		35.8	26.9		34.0	27.6	34.4	26.6	34.6	29.9	36.8	26.8			
Emulsion stability mL																	
oil/mL cream																	
a) O ^a /W = 5/95	2/3	Nil/Nil	0/2	Nil/Nil	Nil/Nil		0/1	Nil/Nil	0/1	Nil/Nil	0/1	Nil/Nil	2/1	Nil/Nil			
b) O/W = 10/90	4/3	Nil/Nil	2/1.5	Nil/Nil	Nil/Nil		0/2	Nil/Nil	0/2	Nil/Nil	0/2	Nil/Nil	2/2	Nil/Nil			

^aO/W = oil/water ratio.

this group, Figure 1(c). The sharp stretching band at 3398 cm^{-1} pointed to alcoholic (OH). The stretching band at 1732 cm^{-1} pointed to the presence of anhydride group (OCOCO), while the stretching band at 1250 cm^{-1} pointed to carbonyl group (OCO), and the stretching band at 2922 cm^{-1} pointed to $(-\text{CH}_2-)$.

Surface Tension and Surface-Active Properties of the Individual Emulsifiers

The critical micelle concentrations (CMCs) of the prepared emulsifiers at 25°C were determined by plotting the surface tension (γ) versus $\ln C$ (solute concentrations). The CMC values were determined from the abrupt change in the slope of (γ) versus $\ln C$ plot (Al-Sabagh et al., 2000); these values are listed in Table 6.

The surface tension (γ_{CMC}) at CMC, the effectiveness of adsorption (π_{CMC}), the maximum surface excess (Γ_{max}), and the minimum area per molecule (A_{min}) were used as parameters to calculate free energy of micellization (ΔG_{mic}) and adsorption (ΔG_{ad}). These thermodynamic parameters were calculated using the following equations (Al-Sabagh et al., 2004), and these values are listed also in Table 6.

$$\pi_{\text{CMC}} = \gamma_0 - \gamma_s \quad [1]$$

where γ_0 is the surface tension of water at workable temperature and γ_s is the surface tension of surfactant solution.

$$\Gamma_{\text{max}} = \left(\frac{1}{RT} \right) \left(\frac{-d\gamma}{d\ln C} \right)_T \quad [2]$$

where R = gas constant 8.314 J/mol , $T = T_C + 273$, and $(-d\gamma/d\ln C)$ is the surface activity (slope of γ versus $-\ln C$).

$$A_{\text{min}} = \frac{10^{16}}{N\Gamma_{\text{max}}} \quad [3]$$

where N is Avogadro's number (6.023×10^{23}).

$$\Delta G_{\text{mic}} = RT \ln \text{CMC} \quad [4]$$

$$\Delta G_{\text{ad}} = RT \ln \text{CMC} - 6.023 \times 10^{-1} \pi_{\text{CMC}} \cdot A_{\text{min}} \quad [5]$$

The γ_{CMC} and ΔG_{ad} were taken to differentiate between the undertaken emulsifiers on the basis of emulsion stability.

The emulsifiers that exhibited more negative values of ΔG_{ad} are able to make strong adsorption on the interface of oil-in-water emulsion (cutting fluids). The more negative values of ΔG_{ad} lead to greater reduction of surface tension, and, further, the maximum stability of emulsion should be obtained so that they stabilize the cutting oil emulsion formulations. The $-\Delta G$ values against the emulsifiers (ABPG(4)S, ABE(9)S, E(22.7)CME, E(13.6)ODME, E(13.6)COM, and E(20)STO) are -22.89 ,

-23.28 , -24.49 , -23.66 , -24.21 , and -25.2 kJ mol^{-1} . From the data of γ_{CMC} in Table 6, it was found that the maximum reduction of surface tension values were 27.4 , 27.0 , 26.8 , 27.4 , 28.6 , and 29.2 mN m^{-1} . These data correspond to the mentioned emulsifiers respectively.

Surface Tension for Some Selected Cutting Oil Formulations

By inspection of the data of surface tension of some formulations as shown in Table 7 it was found that there was a strong relation between emulsion stability and depression of surface tension. From the data given, it was clear that the maximum reduction of surface tension and maximum emulsion stability were exhibited with the following formulation numbers: 4, 5, 10, 12, 16, and 17, which were made by emulsifiers ABPG(4)S, ABE(9)S, E(22.7)CME, E(13.6)ODME, E(13.6)COM, and E(20)STO respectively. Other formulations, 18, 21, 11, 6, 7, and 1, were made by the same emulsifiers respectively, but they exhibited lower reduction of surface tension and emulsion stability than that obtained with the other formulations as listed in Table 7. This means that the synergistic effect between the formulation ingredients and the emulsifier used should be considered.

CONCLUSIONS

- Different emulsifiers were prepared from local raw materials, and they were used to stabilize cutting oil emulsion formulations.
- The emulsifier that exhibited maximum reduction of surface tension gave the more stable cutting oil emulsion formulation.
- The minimum surface tension depends on the $-\Delta G_{\text{ad}}$, which also depends on emulsion stability.
- The cutting oil formulation ingredients should be synergetic to obtain the maximum emulsion stability.

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