Extreme pressure behaviour of newly designed oil-in-water emulsions

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ABSTRACT

Oil-in-water (O/W) emulsions are broadly used in metal-machining processes, where combined lubrication and refrigeration are needed, such as in cutting, rolling, or grinding. These fluids consist of tiny oil droplets in water stabilised by small amounts of emulsifiers, namely surfactants. In an emulsion, oil is responsible for the lubricating properties, whereas water provides heat dissipation and fire resistance. Normally, emulsifiable metalworking oils are used in an oil concentration between 2 and 5 vol. %, depending on the application.

Despite their wide use, the lubrication mechanisms of o/w emulsions have not been fully understood, mainly because of their complexity. Previous studies on oil-in-water emulsions showed that, in order to form thick lubricant films, oil droplets must wet the metal surfaces, displacing water. The ability of oil to wet is strongly dependent on the concentration of surfactant. Surfactant molecules tend to adsorb preferentially at the interface, modifying the nature of the layers adjacent to the metal surfaces and, thus, playing a key role in processes such as wettability, corrosion, or friction, as well as emulsion stability.

The aim of this work is to study the influence of concentration of two different emulsifiers (anionic and non-inonic) on the wettability and extreme pressure properties of an oil-in-water emulsion. A mixture of a synthetic polyalphaolefin and a trimethylol propane ester was used as the base oil, and the concentrations of emulsifiers were below, equal to, and above their critical micellar concentrations (CMC). Extreme pressure tests (ASTM D 2783), which try to simulate the operating conditions of high speeds and pressures taking place in cutting processes, and contact angle measurements were carried out in order to establish a relationship between both properties and to evaluate the performance of these emulsions as lubricants.

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1. INTRODUCTION

It is estimated that about 97% of the work employed in some metal-machining processes such as, for example, cutting, is transformed into heat, being stored the rest of the work in tool or metal chips as residual stresses (Springborn 1967, p.7). This heat arise from the plastic deformation of the metal piece and the friction between the metal piece and the tool, reaching temperature values in the contact area about 1000ºC. Hence, every action focused on reducing the temperature must begin in the reduction of friction and deformation. Oil-in-water emulsions fulfil these observations: the oily phase works as lubricant reducing the friction between workpiece and tool whereas the aqueous phase (about the 95% in weight) helps to dissipate the heat in the contact from 2 to 3 times faster than oil due to its higher specific heat.

Oil-in-water (O/W) emulsions used as metalworking fluids are complex mixtures where, apart from the base oil and water, many additives are present: emulsifiers (*i.e.* surfactants), corrosion inhibitors, antifoaming agents, biocides, extreme pressure additives, etc. The contact area is a tribosystem with two liquid phases (oily and aqueous phases) and a solid phase (the metal surface), with many processes involved − adsorption, desorption, coalescence, starvation − and in conditions of high temperatures and pressures. Moreover, the surfactant molecules, whose name stands for *surface active agents*, tend to adsorb onto the interfaces modifying their properties. Some authors suggest that O/W emulsions must wet the metal surfaces in order to form thick lubricant films in the contact (Kimura and Okada 1989, Ratoi *et al*. 1997a, Ratoi *et al*. 1997b). Other authors remarked the influence of the oil droplet size and emulsion stability in the efficiency of the lubrication (Nakahara *et al*. 1988, Zhu *et al*. 1994, Yang *et al*. 2003). All these interfacial properties depend in a great extent on the surfactant concentration, playing this parameter a key role in the lubrication phenomena. Furthermore, these properties are often conflicting among them. For these reasons, the lubrication mechanism of emulsifiable oils has not been fully understood.

The effect of the concentration of two different surfactants on the extreme pressure behaviour of an oil-in-water emulsion is studied in this work. Surfactant concentrations below, close to and above the critical micelle concentration (CMC) were used. CMC can be defined as the concentration at which the factors which favour the formation of micelles (for instance the hydrophobic effect) start dominating the effects which oppose it. Below the CMC, no micelles are formed and the surfactant molecules remain in solution as monomers or adsorbed on the interfaces. At CMC, the surfactant molecules tend to form aggregates (micelles or bilayers) in which the surfactant hydrophilic groups are oriented towards the bulk aqueous phase whilst hydrophobic groups remain inside the micelles, in order to minimise their interaction with the aqueous phase. At higher concentrations than CMC, monomers and micelles coexist in equilibrium. The different conformations that surfactant molecules can adopt depending on the concentration will determine the interfacial characteristics of a solution or an emulsion and, consequently, its behaviour in a lubricated contact.

2. MATERIALS AND METHODS

2.1. Materials

A mixture of a synthetic polyalphaolefin (PAO-10) and trimethylol propane ester (TMP, 15% w/w) was used as base oil. Two different surfactants were added to stabilise the emulsion:

- Oleth-10, glycolic acid ethoxylate oleyl ether (Sigma-Aldrich, Inc., CMC = 20 mg/L), anionic.
- Brij-76, polyethylene glycol octadecyl ether (Sigma-Aldrich, Inc., CMC = 200 mg/L), nonionic.

The chemical structure of both surfactants is shown in Figure 1. The CMC was determined at 20ºC by surface tension measurements using a Krüss K-8 tensiometer, following the platinum ring method.

All emulsions were prepared with 3% w/w oil content in deionised water (Millipore Elix 5 deioniser) and homogenised for 10 minutes at 15000 rpm using a Heidolph Diax 900 homogeniser. Surfactant concentrations used, referred to the CMC, were the following: 0.25, 0.5, 1.0, 2.0, and 10.0 times the CMC.

a)

$$CH_3 - (CH_2)_x \quad \diagdown C=C \diagup \quad (CH_2)_7 - CH_2 - (OCH_2CH_2)_y - O - CH_2 - COOH$$

x: 5-7
y~9

b)

$$C_{18}H_{37} - (OCH_2CH_2)_x - OH$$

x ~ 10
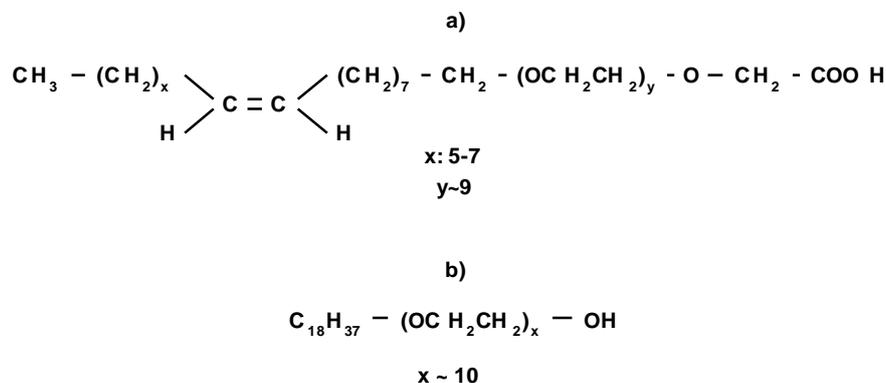
Figure 1. Chemical structure of surfactants: a) Oleth-10, anionic. b) Brij-76, nonionic.

2.2. Extreme pressure tests

Extreme pressure tests were carried out in a Stanhope Seta Shell Four-Ball E.P. Lubricant Tester under the ASTM D 2783 standard. The driving shaft speed was 1470 rpm. The ball test material was 12.7 mm diameter AISI 52100 steel with a hardness of about 65

HRC. The following parameters were calculated from the extreme pressure tests: initial seizure load (ISL), weld load (WL) and load wear index (LWI). Diameter wear scars (DSC) were measured using a Nikon PFX optical microscope with a Nikon F-301 CCD camera which allows to capture images.

From the EP results a number of tribological parameters were determined. For the purpose of illustration the wear-load curve is shown in Figure 2.
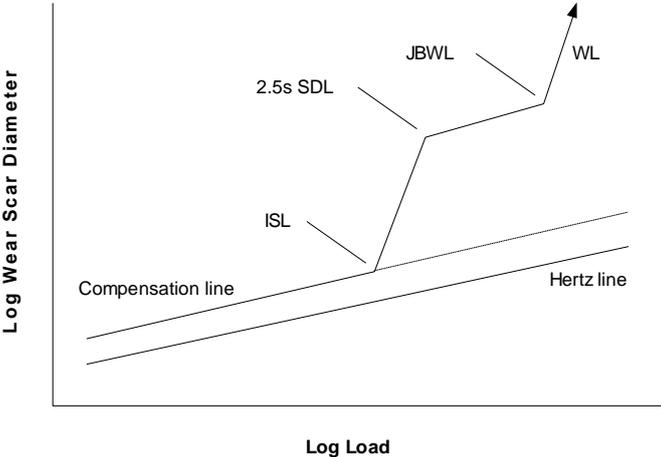
Figure 2. Wear-load curve obtained from the extreme pressure tests.

2.2.1. Hertz line

The Hertz line is obtained by plotting the Hertz scar diameter against the load. The Hertz scar diameter (d_h) is the average diameter of an indentation caused by the deformation of the balls under static conditions.

2.2.2. Compensation line

The compensation line is a line of plot where the coordinates are the compensation scar diameter and the applied load. The compensation scar diameter is the average diameter of the wear scar on the stationary balls caused by the rotating ball under an applied load in the presence of lubricant, but without causing either seizure or welding.

2.2.3. Initial seizure load (ISL)

The initial seizure load or point of non-seizure load is the last load at which the measured scar diameter is not more than 5% above the compensation line.

2.2.4. Weld load (WL)

The weld load (WL) is the lowest applied load at which the rotating ball welds to the three stationary balls.

2.2.5. The 2.5s seizure delay load

The load for which the seizure delay is 2.5 s, provides a reliable method for testing the protection against seizure afforded by the lubricant used.

2.2.6. Load wear index (LWI)

The load wear index (LWI) or mean hertz load (MHL) is a single number that expresses the overall EP behaviour and covers from well below seizure to welding. It may be calculated from the expression:

$$LWI = \frac{\sum_{i=1}^{n} \frac{P_i \, d_{h,i}}{d_i}}{n},$$

where P is the applied load, d_h the Hertz diameter, n the total number of occurrences, and d the wear scar diameter.

2.3. Contact angle measurements

Contact angle is a quantitative measure of the wetting of a solid by a liquid. Low contact angle values indicate that the liquid wets well, while high values indicate poor wetting. A KSV CAM 200 Optical Contact Angle Meter was used to evaluate the wetting properties of the different O/W emulsions. An AISI 1015 steel plate was submerged in solutions of both surfactants and then oil droplets were placed on the metal surface. Images of the S/L/L system were captured by a high resolution CCD camera at a 180-second interval during 30 minutes and contact angle measurements were made using the CAM 200 software.

3. RESULTS AND DISCUSSION

The extreme pressure results of O/W emulsions with the nonionic surfactant Brij-76 and the anionic surfactant Oleth-10 are summarised in Table 1. Experimental results of the base oil and the blends of base oil and the surfactants (0.1% w/w) are also included.

As it can be seen in Table 1, the addition of small amounts of surfactants hardly affect the extreme pressure properties of the base oil. Only a reduction in the wear scar diameter at just before the weld load (JBWL) was observed but the LWI values are rather similar. It is noticeable that the oil emulsification causes lower weld loads regardless of the concentration and type of surfactant. The region beyond the ISL is known as *extreme pressure (EP) region*, whereas the region before the ISL is the *antiwear (AW) region*. In the AW region, a film of lubricant is physically adsorbed on the metal surface and the ISL value is related to the physisorption strength of lubricant on the surface. Surprisingly, some Oleth-10 emulsions had higher ISL values than the base oil. The polar aqueous bulk phase might enhance the electrostatic interactions between the negative-charged surfactant and the steel surface, being more resistant to be removed from the interface.

At the 2.5s SDL, the desorption of this lubricant film takes place due to the increase of temperature in the contact, with a sudden increase in the wear scar diameter values. This lubricant film is not present in the extreme pressure region, so seizure and eventually welding occurs. The addition of some tribologically-active compounds, usually nitrogen-, sulfur- or chlorine-containing substances, delays the welding point by forming a chemical film of inorganic salts ($FeCl_2$, FeS, $FeSO_4$, etc.) which prevents seizure. Figure 3 shows the wear-load curve for lubricants with the best LWI for each group. Contact angle measurements for both surfactants are shown in Table 2.
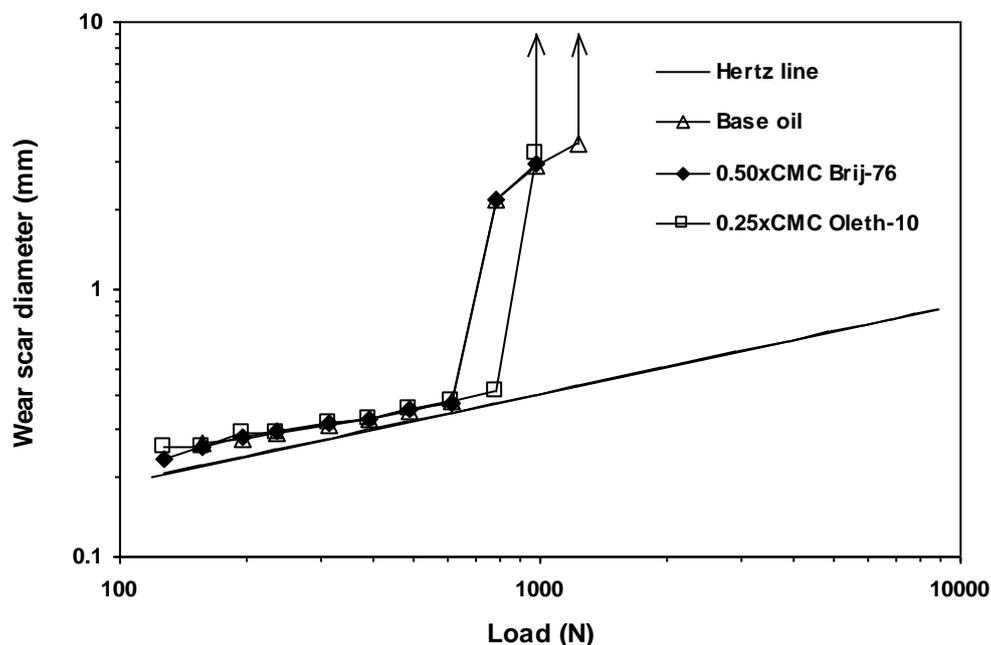
Figure 3. Wear scar diameters versus load for different lubricants tested.

Table 1. Experimental EP results of base oil and O/W emulsions prepared.

Lubricant	Initial seizure load ISL (N)	Mean wear scar diameter at ISL (mm)	Weld load WL (N)	Mean wear scar diameter at just before weld load JBWL (mm)	Load Wear Index LWI (N)
Base oil	617	0.379	1568	3.52	26.4
Base oil + Brij-76 (0.1% w/w)	617	0.373	1568	2.97	27.0
Base oil + Oleth-10 (0.1% w/w)	617	0.371	1568	2.87	27.0
Emulsion, no surfactant	617	0.394	1235	3.62	23.4
Emulsion, 0.25xCMC Brij-76	617	0.386	1235	3.28	25.2
Emulsion, 0.5xCMC Brij-76	617	0.378	1235	2.97	25.8
Emulsion, 1.0xCMC Brij-76	617	0.374	1235	3.19	25.4
Emulsion, 2.0xCMC Brij-76	617	0.372	1235	3.05	25.2
Emulsion, 10.0xCMC Brij-76	617	0.385	1235	3.04	25.7
Emulsion, 0.25xCMC Oleth-10	784	0.415	1235	3.21	31.4
Emulsion, 0.5xCMC Oleth-10	784	0.457	1235	3.26	30.7
Emulsion, 1.0xCMC Oleth-10	617	0.385	1235	2.94	25.3
Emulsion, 2.0xCMC Oleth-10	617	0.379	1235	3.10	25.5
Emulsion, 10.0xCMC Oleth-10	784	0.425	1235	2.88	30.6

Table 2. Contact angle measurements of base oil on a steel plate submerged in surfactant solutions.

Surfactant concentration	Contact angle (º)
No surfactant	120.1
0.25xCMC Brij-76	132.9
0.5xCMC Brij-76	153.7
1.0xCMC Brij-76	163.5
2.0xCMC Brij-76	147.0
10.0xCMC Brij-76	154.0
0.25xCMC Oleth-10	137.3
0.5xCMC Oleth-10	125.4
1.0xCMC Oleth-10	114.2
2.0xCMC Oleth-10	84.0
10.0xCMC Oleth-10	96.0

The use of the anionic surfactant Oleth-10 gave lower contact angles than the nonionic surfactant Brij-76. An unexpected similarity between the contact angle and the load wear index results was found, as it is shown in Figure 4. According to this data, those emulsions with poor wetting characteristics showed better load-carrying properties.

a)   b)
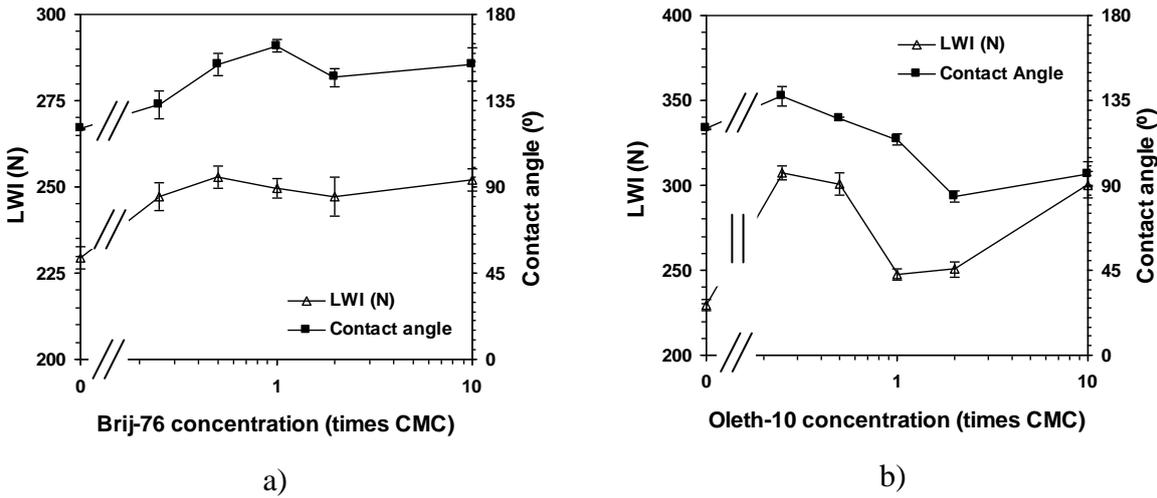
Figure 4. Load wear index (LWI) and contact angle *vs.* surfactant concentration. a) Brij-76, nonionic. b) Oleth-10, anionic.

4. CONCLUSIONS

Oil-in-water emulsions showed an extreme pressure behaviour not far from the EP properties of the base oil. Parameters such as initial seizure load (ISL), weld load (WL) or load wear index (LWI) are close to those found when the base oil was tested without emulsifying. Even the use of an anionic surfactant improved the load-carrying capacity of some emulsions when compared to the neat base oil.

A dependence between the non-wetting properties and the EP behaviour of emulsions was found but, since these parameters affect to another properties involved, specially the emulsion stability, further work is required in order to achieve the best performance of the formulation.

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