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Citation: [AIP Conference Proceedings](#) **1888**, 020006 (2017); doi: 10.1063/1.5004283

View online: <http://dx.doi.org/10.1063/1.5004283>

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Lubrication Studies of Some Type III Deep Eutectic Solvents (DESs)

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Abstract. It has previously been shown that eutectic mixtures of quaternary ammonium salts and hydrogen bond donors form liquids with properties similar to ionic liquids [1; 2]. These so-called deep eutectic solvents (DESs) have been shown to have physical properties which would make them useful as base lubricants. The base lubricant needs to show specific properties, including high viscosity index (VI), low friction coefficient (μ), low pour point and corrosivity. To determine the applicability of DESs as base lubricants, physical properties, corrosion and lubrication properties for four type III DESs have been studied and the results have been compared with mineral base oil. The data show that the lubrication properties of DESs are superior to mineral base oil for short distances. All DESs assessed here have higher VI (191, 147, 121 for Ethaline, Glyceline and Reline respectively compared with 100 for mineral base oil), lower pour points than mineral base oil and most of the liquids studied have shown very low corrosion rates ($< 3 \mu\text{m year}^{-1}$ for mild steel).

INTRODUCTION

A lubricant is a material used to assist the relative motion of sliding bodies by offering a protective thin film between their surfaces in order to reduce wear and friction between contacting sliding surfaces. A major environmental focus is to design environmental friendly lubricants. The hydrophobicity of mineral base oils makes them environmentally incompatible and this is considered as one of the most important reasons to study hydrophilic based lubricants[3; 4]. Therefore, for a specific system a suitable lubricant needs not only a given mechanical durability but it should also have greener credentials than what it is replacing[5].

Using liquids made of or containing ions as a lubricant is quite different from liquids made of hydrocarbons. The later as non-conducting media should inhibit corrosion and most formulated oils contains additives to actively prevent corrosion. On the other hand, high conducting media such as ionic liquids (ILs) or DESs would be thought to behave differently toward metals in contact with them.

The increasing demands in lubricant specification particularly for automotive and aerospace applications have led to improvements in efficiency and performance[6]. Nowadays formulated lubricants based on biodegradable materials for applications such as marine and industrial gear oil, hydraulic fluids and tractor transmission oils are becoming more common[7]. In current study some type (III) DESs have been assessed as base lubricants and their characteristics with the similar properties of mineral base oil are compared. In these studies no additives have been used so that the characteristics of the base material could be considered. This clearly will not produce lubricants which can be compared with commercial products but it provides a baseline for comparison sake.

MATERIALS and METHODS

The DESs prepared using the same method as reported in the literature [8; 9]. Mobil Therm 605 as a standard was used as mineral base oil. The viscosity was measured using both Ubbelohde and rotational (Brookfield DV-II+ Pro) viscometers according to ASTM D445[10] and ASTM D2196[11]. To be suitable as base lubricants fluids need to retain an appropriate viscosity profile over a wide range of temperature. This is generally expressed through the viscosity index (VI) which is defined as;

$$VI = 100 (L-U) / (L-H)$$

Where U is the kinematic viscosity at 40°C of the unknown oil DESs here; L is the kinematic viscosity at 40°C of an oil (VI = 0) having the same viscosity at 100°C as the unknown oil; H is the kinematic viscosity at 40°C of an oil (VI = 100) having the same viscosity at 100°C as the unknown oil[12]. Both density and surface tension were measured using Krüss Tensiometer K9 model K9MK1. Wettability represented by contact angle measurements were done using CAM 100 contact-angle meter from (Edmund industrial optics). The corrosion studies were carried out using AUTOLAB instruments (Autolab PGSTAT12). In all experiments the metal samples (Al, Fe and Ni) were used as a working electrode and Pt electrode as a counter electrode and the reference electrode was (Ag/AgCl 1 M KCl). For measurement of corrosion rates electrodes were polished with alumina (0.05 µm) before each experiment. Corrosion rates were calculated using ASTM G 59-97. where i_{corr} is the corrosion current density, B is the Stern–Geary constant and R_p is the polarisation resistance. The value of i_{corr} was obtained automatically from software and converted to corrosion rates by means of equivalent weights and density values for each metal in LSV after adjusting for the surface area (cm²) of a metal electrode.

RESULTS AND DISCUSSION

In the current study four DESs were tested at their eutectic composition using choline chloride (ChCl) with different hydrogen bond donors (acids, alcohols and amides). Table (1) shows some physical properties such as density, freezing point and viscosity index data for four DESs and mineral base oil. All DESs have viscosity indexes which are above the value of the base oil. Most of the DESs also have improved freezing points compared to the base oil suggesting improved performance at lower temperatures. The urea based eutectic with choline chloride has too high a freezing point and coupled with the propensity for urea to break down to form ammonia at high temperatures would probably make it unsuitable for general use. The glycol based liquids are, however better at both high and low temperatures and have high VI values. The benign nature, particularly of glycerol, makes this eutectic an interesting candidate for a marine lubricant because it is totally miscible with water and would disperse if discharged at sea. Since both components are extremely benign they pose negligible threat to aquatic life. Generally, all DESs here are denser than mineral base oil which requires pumping consideration during their application.

If DESs are to be suitable base lubricants their corrosion behaviour needs to be characterised for different metals and alloys that they are expected to be exposed to during their service. Table (2) and Figure (1) shows initial corrosion data for four DESs.

TABLE 1. *Physical properties data of liquids.*

Fluid	Density at 298K /g cm ⁻³	Viscosity /mm ² s ⁻¹		Viscosity Index	Pour point K
		at 40°C	at 100°C		
Base oil	0.87	30	5	100	267
Ethaline	1.12	20	5	191	215
Glyceline	1.19	118	23	147	241
Reline	1.20	218	24	121	288
Oxaline	1.20	149	28	144	258

It is well known that chloride ions can significantly enhance the corrosion rate in aqueous solution as they break down passive films.[13; 14] As such it would seem logical that chloride based DESs should be avoided for lubricant applications.

TABLE 2. Corrosion rates of mild steel in different liquids at 298 K.

Fluid	Corrosion rate measured by LSV of mild steel / $\mu\text{m year}^{-1}$
Ethaline	1.90
Glyceline	0.40
Reline	2.50
Oxaline	176

The corrosion rates are particularly low for Ethaline, Reline and Glyceline however, extremely high for Oxaline. The origin of this difference could be due to the presence of an insulating film on the metal surface or the kinetics of either the anodic or cathodic processes.

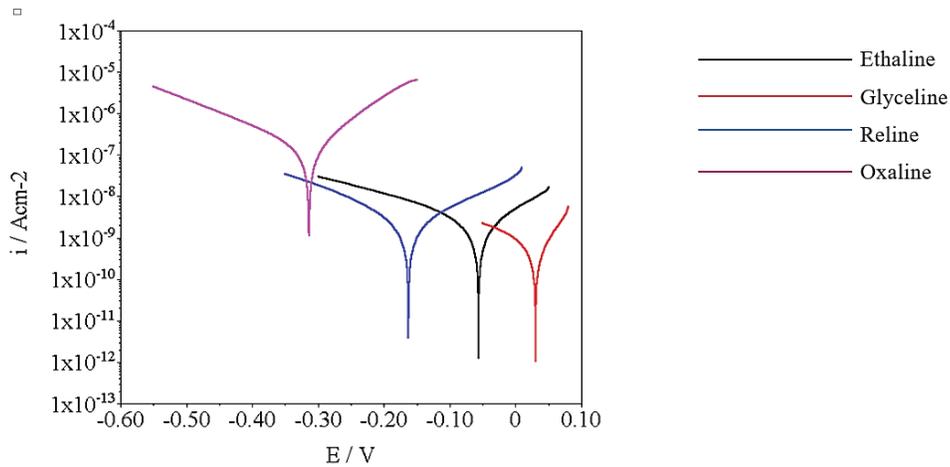


FIGURE 1. Polarization curves for a iron in Ethaline, Glyceline, Reline and Oxaline at 298K.

Corrosion rates as shown in Table (2) determined using Tafel slopes from slow-rate linear sweep voltammetry (LSV) for mild steel in some DESs.

Figure (1) shows the Tafel slopes in Ethaline, Reline and Glyceline the cathodic slope is shallow in comparison with Tafel slope for Oxaline suggesting that the cathodic process is rate limiting. In these liquids the cathodic process is the reduction of oxygen i.e.



Previously it has been shown that the addition of quaternary ammonium salts lead to a decrease in the friction coefficient of fluids and the minimum friction occurs at the eutectic composition[2].

Figure (2) shows the measured friction coefficient for DESs and mineral base oil for steel/steel couples.

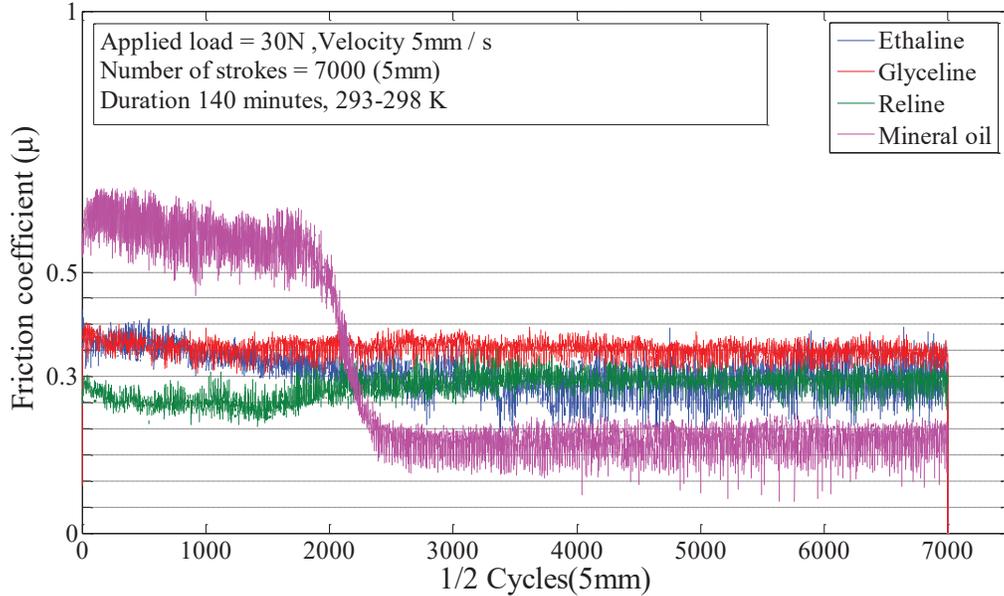


FIGURE 2. Friction coefficient for three DESs and mineral base oil using stainless steel substrate.

It should be highlighted that this study is comparing the properties of the ionic fluids to those of the base lubricating fluid. The properties of finished lubricating fluids are usually superior to those studied here due to complex additive packages.

The average frictional coefficients for various DESs and mineral base oil with different sliding surfaces are summarized in Table (3). The data in the table are measured under the following condition; number of strokes are 2000, applied load was 30N and reciprocating velocity was 5mm/s at 293-298K.

As shown in Table (3) the friction coefficients for DESs are lower than for the mineral base oil with mild and stainless steel, but they are slightly higher values for the aluminium couples.

However as shown in Figure (2) after 2000 strokes the behaviour of mineral base oil changed for steel/steel couples with a decrease in friction coefficient. The reason for this is not fully understood but it could be due to initial increased wear which produces a smoother surface which oil can wet better. In the beginning the oil may wet the surface poorly but it may become more entrapped with wear.

TABLE 3. Friction coefficient data of different contact pairs under 30 N load at 298 K.

ILs	Friction coefficient (Substrate metals against stainless steel)				
	Al	Bronze	Cu	Mild Steel	Stainless Steel
Ethaline	0.15	0.58	0.59	0.30	0.31
Glyceline	0.55	0.40	0.45	0.28	0.35
Reline	0.31	0.26	0.21	0.32	0.30
Oxaline	0.25	0.29	0.18	0.38	0.30
Base oil	0.12	0.23	0.37	0.40	0.55

It has been shown before that adding quaternary ammonium electrolytes to ethylene glycol can significantly reduce the friction coefficient which shows that the ionic component has an interfacial preference which allows it to interact with the metal and produce an interfacial barrier. It was found that the friction coefficient was also dependent upon the concentration of quaternary ammonium salt and the optimum lubrication was obtained at the eutectic composition[2].

The efficacy of a liquid lubricant depends upon its interaction with a surface. For example a mineral base oil is made from a mixture of hydrocarbon molecules including saturates (normal straight chains or branched molecules), naphthenic molecules and some aromatic hydrocarbons. The interactions of these kinds of molecules with the metal surface are in general quite weak comprising only van der Waals interactions and do not guarantee strong adhesion of the hydrocarbon to the surface. Consequently, the separation of surfaces from

each other by additive free mineral base oil is only possible for lightly loaded surfaces due to the ease of removing the liquid from the surface.

In contrast to the hydrophilic molecules in mineral oils, DESs should have much stronger interactions with most metallic surfaces. The inter-molecular and inter-ionic interactions in DESs are much larger than the van der Waals attractive forces into mineral oils. The presence of polar functional groups such as OH, CONH₂ and COOH in DESs will enable adsorption on the surface through either by hydrogen bonding or chemical reaction with surface consequently forming a thin layer of a lubricant on the surface and reducing friction and wear as well[15].

CONCLUSIONS

In summary, the lubrication of a surface is influenced by both intermolecular interactions which determines how the liquid behaves thermally and with mechanical forces and by the interaction of liquid with the lubricated surface. This explains why there is a disparity between the friction constant reported in this study. The corrosion rates for iron in Glyceline and Reline are small and remain almost constant overtime which is due to slow cathodic reaction rates resulting from different processes occurring due to differences in pH.

ACKNOWLEDGMENT

The authors would like to acknowledge the higher committee for education development in Iraq (HCED) for funding studentship. We would also like to thank the university of Leicester for using their equipments.

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