

## The study of activation energy of corrosion in eutectic mixture base lubricants

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**Abstract:** Due to the difference in the ionic nature of mineral base oil and Deep Eutectic Solvents (DESs), corrosion studies of base lubricants based on DESs should be addressed while their lubrication studies are performed. The activation energy ( $E_a$ ) of corrosion for iron are determined in Ethaline (ethylene glycol + choline chloride), Glyceline (glycerol + choline chloride), Reline (urea + choline chloride) and Oxaline (oxalic acid + choline chloride). Corrosion current densities ( $i_{\text{corr}}$ ) are measured at 298K, 303K, 313K, 323K, 333K and 343K using linear sweep voltammetry (LSV).  $i_{\text{corr}}$  are extracted from Tafel potential - current plots, then other plots between  $\ln i_{\text{corr}}$  against  $1/T$  have been made. Finally,  $E_a$  are determined from the slope of plots between  $i_{\text{corr}}$  and  $1/T$ . These values represent how iron corrodes in these liquids if they are heated while applied as lubricants. It was found that the energy of activation of iron in these liquids follows their easiness of hydroxyl proton loss which occurs during their heating.

**Keywords:** Lubricants, DESs, activation energy, corrosion, current density

### 1. Introduction

The cost and toxicity are considered as the most important issues in chemistry to characterise and develop new liquids. In this regard, Ionic liquids (ILs) and Deep Eutectic Solvents (DESs) have shown remarkable promise in the recent years. In Comparison with popular organic solvents, due to having low toxicity, high chemical and thermal stability, negligible vapor pressure, high conductivity, wide potential window and solubility of various inorganic and organic compounds, studying ILs are considered as most developed area in chemistry.[1-3] Evaluating tribological and lubrication properties of ILs dates back to early years of the new millennia[4] and a number of reviews are available concerning this subject.[5-7]

DESs are widely recognized as a new class of IL analogues because they share many properties and characteristics with ILs, however, they are totally different liquids.[2] Compared to ionic liquids, DESs are much less toxic, cheaper to prepare, generally biodegradable and are non-flammable.[8] Therefore, in the past decade as cost-effective ionic liquid analogues, the use of deep eutectic solvents (DESs) has attracted growing attention.[3; 9]

Most important application areas of DESs includes primarily as separation or reaction media, catalyst, alternative electrolytes, lubricants and others. The first paper concerning the

study of lubrication and tribological properties of DESs, have been published in 2010.[10] However, the paper did not cover the subject in detail to include most metal free DESs with various metal substrates. Therefore, a very detailed study have been done later to cover the study of thermo-physical, rheological, mechanical and corrosion behaviour of type III DESs.[11]

The aim of this study is to determine the activation energy of corrosion for the first time, in four DESs using corrosion current densities as a function of temperature to show how corrosion going to be change if DESs are used as base lubricant and heated during the use.

## **2. Experiments and Chemicals**

All chemical were used as received from the suppliers. DESs were prepared as follows:[11] Glyceline (choline chloride 1:2 glycerol) molar ratio was prepared by mixing and heating at *c.a.* 353 K, until a clear liquid was formed. Ethaline was prepared by the same procedure however, ethylene glycol instead of glycerol has been used and heating was at 333 K.

For Reline the same molar ratio (choline chloride 1:2 urea) was used, and then the mixture was stirred periodically in an oven at 320 K until a clear liquid was formed. Oxaline on the other hand, was prepared using the procedure for Reline, but the molar ratio of a mixture was (ChCl 1:1Oxalic acid).

AUTOLAB instruments (Autolab PGSTAT12) was used to measure all corrosion data. In all recorded data the disc shape working electrode was made from the metal being studied and a counter electrode was Pt electrode, however, the (Ag/AgCl in 1 M KCl concentration) used as reference electrode. For every single experiment when corrosion current measured the electrodes were polished firstly with 0.05  $\mu\text{m}$  alumina then it was placed in a liquid at specified temperature and left for at least 15 minutes to reach the temperature of the bath.

## **3. Results and discussions**

Essentially, the process of corrosion is a surface phenomenon; accordingly valuable information concerning the interactions of a metal surface with the surround could be extracted by studying the physical chemistry of a metal surface. Commonly, Arrhenius equation, which relates temperature with measured corrosion current density, is employed to calculate activation energy of corrosion as shown below:[12]

$$i_{corrosion} = e^{(-E_a/RT)}$$

Where;

$E_a$  is the activation energy. Since T and  $i_{corrosion}$  are measurable values,  $E_a$  could be calculated from the slope of  $-\ln i_{corr}$  and  $1/T$  graph as shown in (Figure 1) for instance.

Corrosion current densities for iron in four different DESs as a function of temperature are shown in Table 1.

Most chemical reactions are accelerated with increase in temperature. As shown in the table the corrosion current densities of iron are quite different in DESs. This is thought mostly to be connected to the loss of hydroxyl proton in the case of Ethaline, Glyceline and Oxaline. As reported before[3] for water and DESs mixtures, the OH on both hydrogen bond donors (ethylene glycol, glycerol and oxalic acid) and choline cation behaves differently. In Ethaline and Oxaline already the proton loss is easier than in Glyceline which are forming acidic mixtures in the presence of water, however for Glyceline the dissociation slightly is smaller. This behaviour is responsible for the increase in cathodic reaction rate which increases the

rate of anodic reaction as well. This tendency is clearly shown in Table 1 as the temperature was increased the corrosion current increased too.

Table 2 shows activation energy of corrosion of iron in liquids mentioned before. With similar trend of corrosion current densities, a value of activation energy of corrosion depends greatly on the association and dissociation of hydroxyl proton on groups, hydrogen bond donors and hydrogen bond acceptor.

#### 4. Conclusion

This study has shown that the current densities of iron in DESs increase with increase in temperature. The activation energies of corrosion of iron particularly in those liquids based on HBDs containing hydroxyl group, together with choline chloride have the activation energies which corresponds to how difficult the hydroxyl proton dissociates. The proton in Oxaline, which loses easier than in other liquids, shows bigger activation energy. Reline behaves differently in comparison with other liquids; it is not clear in this stage, why it behaves in this manner.

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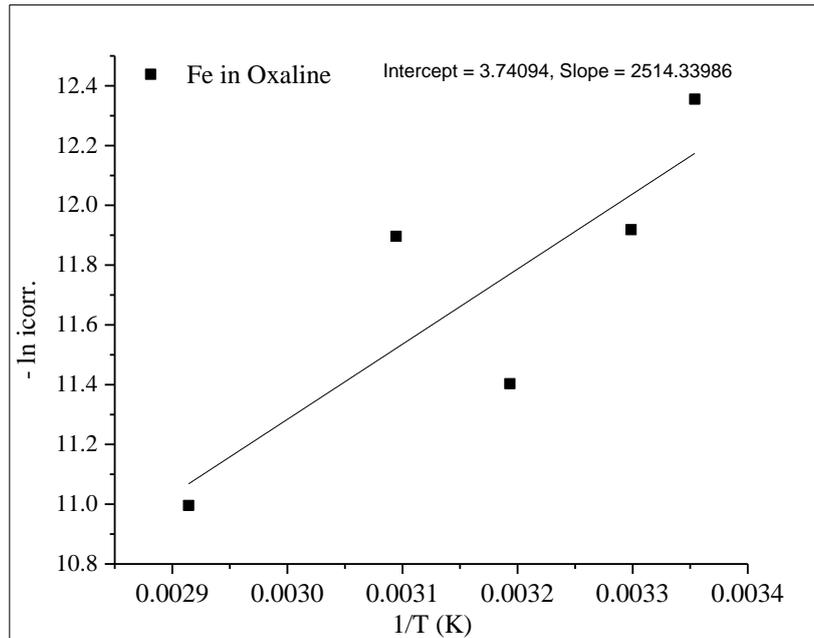
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**Table 1:** Corrosion current densities of iron in DESs as a function of T.

T/K	<b>I<sub>corr.</sub> of iron in different DESs</b>			
	<b>Ethaline</b>	<b>Glyceline</b>	<b>Reline</b>	<b>Oxaline</b>
298	1.202E-06	9.211E-07	6.949E-08	4.307E-6
303	2.231E-6	1.53633E-06	2.80667E-06	6.666E-6
313	1.257E-6	1.36533E-06	2.705E-08	1.116E-5
323	1.4235E-06	1.36533E-06	2.9635E-08	6.81633E-06
333	1.9055E-06	3.321E-08	5.553E-08	.....
343	1.784E-6	2.21667E-06	2.74E-7	1.677E-5

**Table (2) activation energies of iron in four DESs.**

<b>DESs</b>	<b>Slopes</b>	<b>Ea / kJ.mol<sup>-1</sup></b>
<b>Ethaline</b>	923.00218	7673.840125
<b>Glyceline</b>	1967.58437	16358.49645
<b>Reline</b>	-6302.78893	-52401.38716
<b>Oxaline</b>	2514.33986	20904.2216



**Figure (1): The plot of natural log of corrosion current density as a function of temperature for iron in Oxaline.**