THE TRIBOCHEMICAL REACTIONS OF LOW MOLECULAR ALCOHOLS UNDER BOUNDARY LUBRICATION

Mufid Obadi
Universty of Hodeida, Faculty of Education,
Department of Chemistry. Yemen

Mohamed Al-Nozili
Chemistry Department, Faculty of Science,
Ibb University, Yemen

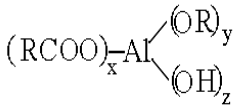
Abstract

Tribochemistry of alcohols is very complex and important from the practical point of view. This paper relates to the research aiming at better understanding of aliphatic alcohol Tribochemistry. Using mostly steel ball-on-aluminum disc friction system, experiments were carried out to generate tribochemical reactions on the aluminum disc. FTIR surface analyses was use analyze the formed deposits. It show anew absorption bands mostly in the region of 1530-1550 cm-1. They are assigned to the specific structure of organometalic compounds which –in many cases- include double bonding in the region of 1600-1650 cm-1. It was also found that the dissociation constant (pKa) values of C1-C4 alcohols control the steel ball wear for both steel-on-steel and steel-on-aluminum systems.

INTRODUCTION

Aliphatic alcohols, similary as alcanoic acids, have long been recognized to be effective antifriction and antiwear lubricant additives. Fatty alcohols, alcanodiols and pentaerythritol partial esters are good examples of boundary lubricants for aluminum. Tribochemical reactions of these additives with aluminum are very interesting, particulary from the view – point of organometalic products resulting from alcohols [1,2,3]. Hironaka and Sakurai found that the caprylic partial ester of pentaerylthritol reacts with surface aluminum atoms to form an amorphous substance such as an complex or salt, during lubrication. This reaction product is an effective antiwear agent for aluminum. Chambat et al. [4] described the products resulting from tribochemical reactions between aluminum and the lubricant

containing fatty acids and alcohols as additives. It was suggested that during plastic deformation fatty acids react directly with aluminum yielding polymeric soaps. Fatty alcohols can lead to similar reaction but on a smaller scale. In this case, a part of the alcohol was assumed to be changed into acid which can react to give an ester and a blend of hybrid soaps of general formula.



Where x= 1, 2 or 3 and x + y + z = 3

The above reviewed literature clearly demonstrated that hydroxyl groups present in a wide variety of compounds do react with aluminum under boundary lubrication conditions. To explain the chemical behaviour of fatty alcohols and other compounds containing hydroxyl groups in sliding contact of aluminum-steel surfaces., Kajdas [5] proposed that the negative-ion-radical action mechanism (NIRAM). The lubrication model is based upon the ionization mechanism of alcohols caused by the action of low energy electrons (2-4eV) emission process from aluminum surface.

Obadi et al. [6] investigated the influence of temperature on wear of the steel ball sliding on steel disk, lubricated with individual alcohols 1-decanol C_{10}, 1-dodecanol C_{12} and equimolar mixtures of these alcohols were found. FTIR surface analysis after friction process presents 1- decanol new absorption bands mostly in the region of 1522 – 1549 cm^{-1} which usually is combined with the absorption bands around 1653 – 1680 cm^{-1} were found in deposits formed on the steel substrates. They have been assigned to organometallic compounds including double bonding.

Research described in the present work relates to Tribochemistry of aliphatic alcohols C_1-C_4 and wear behaviour of C_1-C_8 alcohols and aims at providing more information on and better understanding of steel-on-aluminum wear process lubricated with these compounds. Thus, the primary objective of this paper is twofold (i) to determine the influence of these alcohols on steel mating element wear, and (ii) to elucidate tribochemical reaction of C_1-C_4 alcohols proceeding on the aluminum mating elements under similar test conditions.

EXPERMENTAL TECHNIQUE

Apparatus and lubricants

All the tribological tests were performed with a pin-on-disc tribometer. The apparatuse used was Tester T-01M made in Radom, Poland. Steel ball-on-aluminum disc mating elements used to carry out tests under boundary lubrication conditions. Balls were made from bearing steel LH15 (AISI 52100). Discs were machined from aluminum PA6. The specimens were clamped in place with stainless steel holders. The lower holder contained the lubricant fully flooding the contact region. A dead – weight-loading system applied the normal force. Pure alcohols C_1-C_8 were selected as lubricants for this research. Table 1. lists some properties of the tested alcohols.

Table 1. ***Selected properties of the tested alcohols.***

Alcohol name	Boiling point,	Solubility in water g/ 100g H2O	Dissociation constant, pK_a
Methanol	64.7	∞	15.5
Ethanol	78.3	∞	15.9
1-propanol	97.2	∞	16.10
Isopropanol	81	∞	17.10
t-butanol	82	∞	19.20
1-butanol	117.9	9	
Isobutanol	107	-	
1-pentanol	137.8	2.7	
1-hexanol	155.7	0.6	
1-heptanol	176.3	0.18	
1-oktanol	194.5	0.059	

Test conditions and the procedure

Lubricants comprising pure alcohols were tested under the same operating conditions. Table 2 summarizes test conditions. The test conditions were designed to result in boundary lubrication at sliding interface. Prior to use the steel and aluminum specimens were ultrasonically cleaned in acetone for 20 minutes. Minimum three tests were performed for each alcohol tested. The seals were cleaned before testing the next alcohol. The ball wear scar diameter was measured after unloading the specimens, using a optical microscope.

Table 2. ***Experimental set-up and conditions***

Material system	Steel-on-aluminum
Geometry	Ball-on-Flat
Specimens: Ball	3,18 mm diameter 63 HRC bearing steel R_a = 0,3-0,35
Disc	25,4 mm diameter aluminum PA6 7 mm thickness R_a = 0,5÷0,55 μm
Applied load	9.81N
Wear track radius	8 mm
Sliding velocity	0,250 m/s
Sliding distance	500 m
Temperature	25 ^{0}C

Surface analysis

Infrared spectra of aluminum disc wear tracks were obtained using an infrared microscope coupled to FTIR spectrometer. The used instrument was Perkin-Elmer i-Series Microspectrophotometer. Reflection FTIR spectra were recorded by scanning in selected regions. The spectrometer was operated in mid-infrared frequency range (4000-580 cm^{-1}) at the resolution of 4 cm^{-1} and signal-averaged over 100 scans for background and disc. Perkin-Elmer software IMAGE application allowed to generate spectra at any point of scanned surface. All obtained spectra were corrected by zapping of spurious bands, originated from carbon dioxide and water vapour, smoothing of each spectrum by Savitsky-Golay method and multipoint normalizing of base line using Perkin-Elmer software GRAMS 2000.

RESULTS AND DICUSSION

Wear results obtained in the present work for the steel-on-aluminum material system are collected in table 3, and depicted in figure 1

The found relationship of the steel ball WSD versus alcohol chain length presents a curve composed of two specific elements. The first one representing points for methanol, ethanol, and 1-propanol is a straight line. The second element of the curve is exponential. Zero wear for the 1-hexanol is already very small, reaching only about 0.04 mm. Interestingly, the points corresponding to the WSDs of isopropanol (isopropanol shows lower wear) or 1-butanol, for which the WSD is located below the isobutanol's WSD.

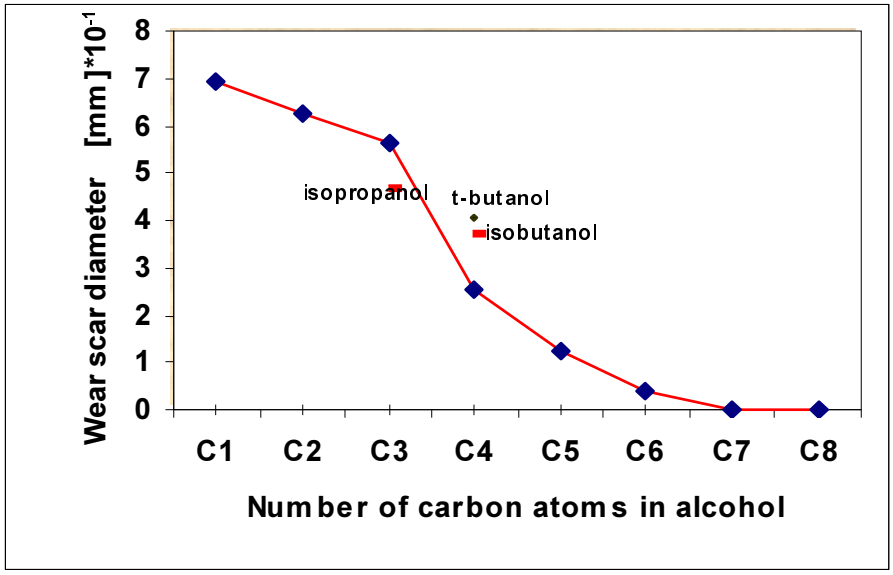


Figure 1. influence of aliphatic alcohol chain length on steel ball wear sliding on aluminum disc.

Table 3. Ball wear scar diameters (WSD) lubricated with pure aliphatic alcohols C_1-C_8

Alcohol name	Carbon number of the alcohol molecule	Wear scar diameter [mm] 10^{-1}	Standard deviation
Methanol	1	6, 92	1.15
Ethanol	2	6. 24	1.22
1-Propanol	3	5.64	1.06
isopropanol	4	4.66	0.56
Butanol	4	2.51	1.16
isobutanol	4	3.72	0.72
1-Pentano1	5	1.23	0.86
1-Hexanol	6	0.42	0.97
1-Heptanol	7	0	0
1-Octanol	8	0	0

Tribochemical reaction of alcohols with aluminum

To investigate the aluminum surfaces from the tribological experiments, FTIR microanalysis (MA) was applied. Chemical information can be obtained on molecular level, including qualitative molecular structure. FTIRMA is non-destructive and rapid, and no special sample preparation is required for that technique. Target spot size in FTIRMA are of the order of 10 micrometer in diameter well within geometry of the wear tracks. The amount of mass that can be detected within these small target areas is of the order of sub-nanogram levels. Comparison of the standerd alcohol absorption bands [7,8] and those found in spectra taken from aluminum wear tracks lubricated by methanol and ethanol differ dramatically, for example, a very strong absorption band at 1615 cm^{-1} in methanol lubricated wear track was found. This peak can be assigned for compounds with dobele bonding. At this point the question arises how unsaturated compounds can be generated from methanol under the used friction conditions? This was absolutely unexpected, because we have not found any refernce suggesting the formation of such compounds from methanol under steel-on-aluminum sliding conditions.

Another peak is observed at 1529 cm^{-1}. The spectrum taken from the wear track lubricated by ethanol shows some similar absorption bands at 1599 cm^{-1} and 1531 cm^{-1}. The first one can be assigned to C=C double bonding combined with oxygen atom C=C-O [8].

Based on the IR refernce table [7,8] peaks at 1529 cm^{-1} and 1531 cm^{-1} can only be assigned for nitrogen containing compounds. To find out some information concerning compounds formed on the aluminum surface from methanol and ethanol, expirment was carried out using glycerol monoacetate. FIG. 2 present the FTIR spectrum taken from wear track lubricated wiyh glycerol monoacetate. The most interesting finding is that this spectrum includes both expexted absorption

bands. For glycerol monoacetate these peaks are shifted to higher wave numbers in comparison to those observed for methanol and ethanol.

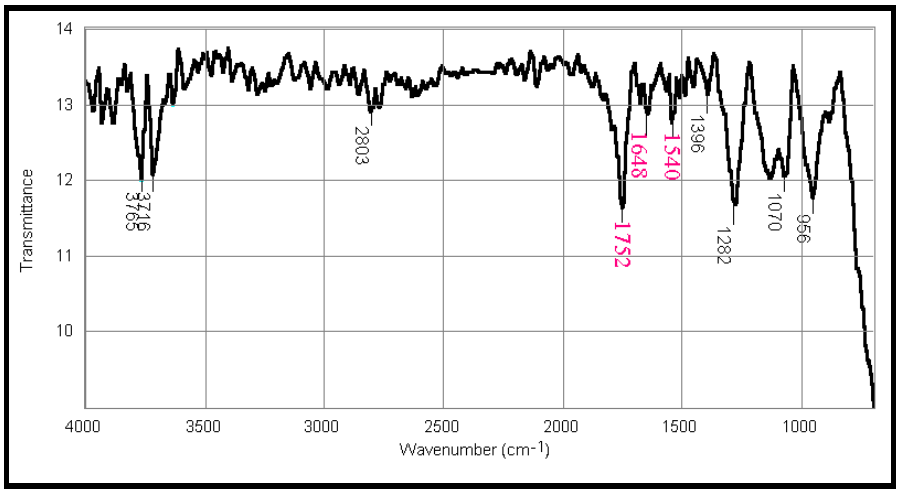


Figure 2. FTIR specrum taken from the aluminum wear track lubricated with glycerol monoacetate.

Actually, they are located at 1540, instead of 1529 and 1531 for methanol and ethanol, respectively, and 1648 cm^{-1}see FIG. 2). Other absorption bands including the peak at 1752 cm^{-1} (C=O ester strech), allowed to sugest the cuclic organometallic compound formed from glycerol acetate with aluminum andur boundary lubrication conditions as shown in FIG 3.

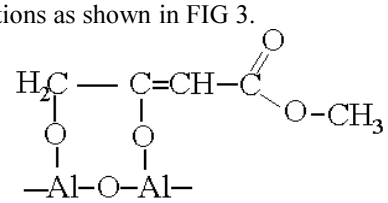
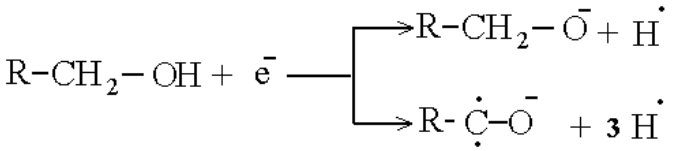
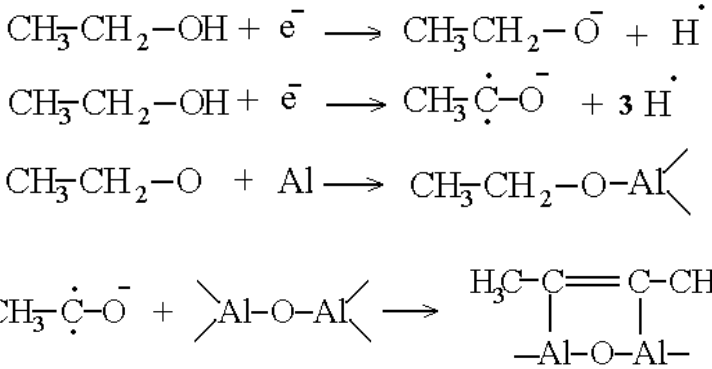


Figure 3. Chemical structure of the major compound formed from glycerol monoacetate on aluminum surface under boundary lubrication conditions.

To account for the triboreaction mechanism of methanol and ethanol to form cyclic organometallics with aluminum, the NIRAM approach is applied. According to this approach [5], low-energy electrons emitted from aluminum surface under boundary lubrication conditions interact with alcohols forming negative ions and negative-ion-radicals. Melton and Rudolph [9] demonstrated formation of the following reactive species from alcohols under the interaction with low-energy electrons:



Accordingly, the tribochemical process of steel-on-aluminum lubricated with ethanol may proceed as follows:



Another reference [10] shows that higher molecular weight fatty alcohols interacting with low-energy electrons also decompose by splitting off two hydrogen atoms producing a radical-anion species R-CH-O-. this was discussed in detail on paper [11]. Thus, R-CH-O- reactive intermediates can also form saturated cyclic organometallic compounds. The same approach leads to similar saturated and unsaturated organometallic structures formed on the aluminum substrate under boundary friction lubricated with methanol. FTIR specter taken from the aluminum surface lubricated with methanol include other peaks for example, around 860, 1090 and the region of 1400 cm^{-1} to 1450 cm^{-1}. Some of them may relate to structures. However, at the present time we don't have enough data to discuss in detail all possible organometallic compounds formed from methanol and aluminum under boundary lubrication conditions. The same is due for other alcohols. An example of the complex tribochemistry of alcohols is shown in FIG. 4, presenting a FTIRMA spectrum of the aluminum wear scar ricatin with isobutanol.

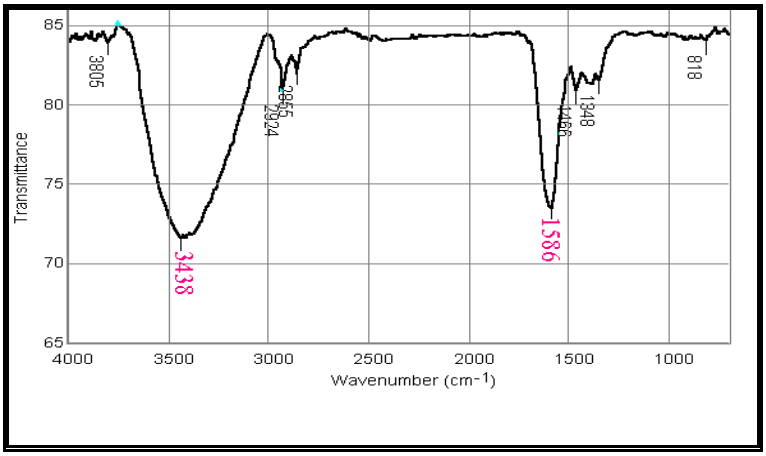


Figure 4. FTIR spectrum taken from the auminum wear track lubricated with isobutanol.

The wear scar After the test was rinsed with n-hexane. This spectrum clearly shows the soap formation along with the presence of OH grups.
FIG. 5 shows another FTIRMA spectrum taken from the same disc after acetone rising. Interestingly this spectrum does not show the –OH group presence. Thus it is possible to conclude that the -OH groups shown in figure 4 relate to physically adsorbed isobutanol molecules attached to the carboxylate oxygen atoms the air hydrogen bonding.

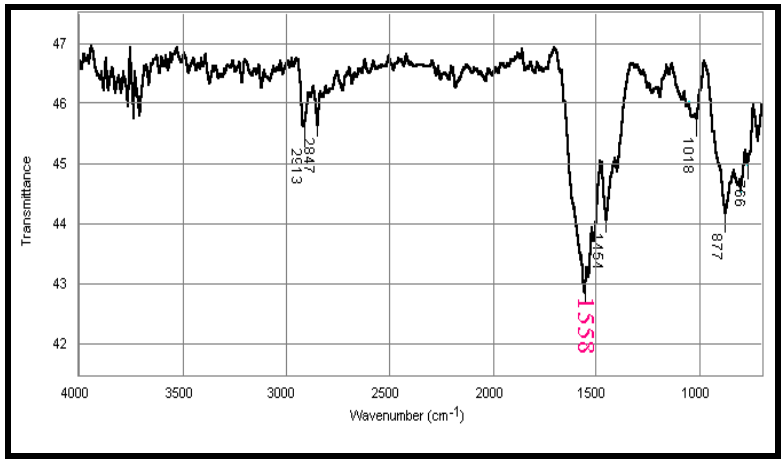
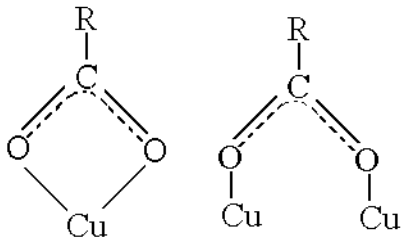


Figure 5. FTIR specrum taken from the auminum wear track lubricated with isobutanol after the disc was rinsed with aceton.

By and large, now it can only be concluded that the tribochemistry of alcohols is probably even more complex than the chemistry of alkoxides being already investigated all were 100 years. It is to not at this end that IR absorption bands in the

range of 1535-1585 cm^{-1} are also characterstic for copper surface lubricated with a 0.4% stearic acid in hexadecane[12], However the intensity of the speaks is very low. The band at 1585 cm^{-1} is assigned to copper carboxylate (RCOOCu) and the bands at 1555 cm^{-1} and 1560 cm^{-1} to the following structures respectively.



Thus it is possible to say that the above structures evidence somehow the structures elucidated in the present paper. In this case corresponding absorption bands are 1529 cm^{-1} for methanol, 1531 cm^{-1} for ethanol and 1540 cm^{-1} for glycerol monoacetate.

Steel ball wear of the steel on aluminum and steel-on-steel systems

Additional tests were performed for methanol, ethanol, propanol, isopropanol, and tert-butanol on the steel-on-steel system under the same other operating conditions as given in table 2. Only these alcohols were selected for the additional tests because we could not find in the enviable references pK_a data for higher molecular weight alcohols. The found in [13] data are given a table one figure sex presents the relationship between the steel bowl ball than WSD and pK_a values and of the alcohols used as lubricants for both steel-on-steel (carve I) and steel-on-aluminum (curve II) system. Based on the obtained results, depicted in figure 2, it can be concluded that pK_a value of the investigated alcohols is a significant factor controlling the steel wear for deferent metal/metal systems lubricated with these alcohols.

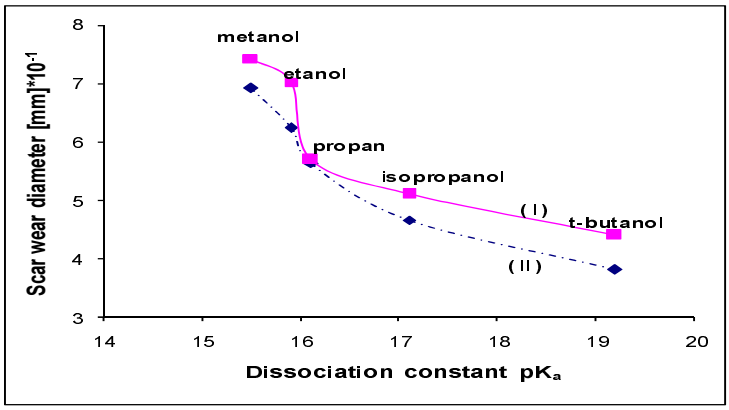


Figure 6. Relationship between the steel ball wear of steel-on-steel (I) and steel-on-aluminum (II) system and the dissociation constant of the applied lubricant.

CONELUSIONS

Using a steel ball on aluminum disc geometry under boundary friction condition lubricated with low-molecular alcohols, a study was carried out on (i) wear behavior of the steel ball and (ii) tribochemistry of methanol and ethanol . It was found that low-molecular weight alcohols cause significant wear of the steel ball sliding on aluminum. Zero steel wear is observed for 1-heptanol (C_7). Additional tests were performed for the Steel-on-steel system lubricated with C_1 to C_4 alcohols. It was found that the alcohols dissociation constant (pK_a) values of the tested alcohols control the steel ball wear for both steel/ aluminum and Steel/steel systems Lubricated with these alcohols.

Another important finding concerns the tribochemistry of alcohols using FTIR surface analysis new absorption bands were found encompass mostly the region of 1530-1550 cm^{-1} which, in many cases, is strictly combined with absorption peaks around 1600-1650 cm^{-1}. They are assigned to organometallic compounds including double bonding. This finding clearly confirm tribochemical reactions of alcohols as proposed in [5]

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