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Tribochemistry of monomolecular lubricant films of ethanolamine oligomers

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ABSTRACT

The aim of present study was to find out the influence of oxygen and nitrogen containing ethanolamine oligomers on the tribological behavior. X-ray photoelectron spectroscopy (XPS) was used to obtain insight into the molecular mechanisms leading to the macroscopic lubricity. Monomolecular lubricant films were deposited onto ultra thin copper films sputtered onto silicon wafers. Surfaces covered with the three ethanolamine oligomers were investigated by XPS before and after tribological tests, performed with the translatorily oscillating test machine and Falex micro-tribometer.

The structure of the molecular film is elucidated using angular resolved X-ray photoelectron spectroscopy with a prototype preparation chamber, permitting the transfer of samples from liquid to the analysis chamber under Helium protective gas preventing exposure to ambient conditions. Solutions with a concentration of 250 ppm of the respective ethanolamine oligomers in double distilled water were transferred into the adsorption device, which is an extension of the spectrometer. Results show that compounds bond to copper and steel surface by N atom present in ammonia group and hydroxyl group are oriented on the top layer of tribofilm, this highest group influence lubricity properties.

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1. Introduction

Additives are of crucial importance in lubrication technology. Additive molecules physisorbed or chemisorbed onto surfaces form lubricating films fundamentally influencing wear and friction properties of two rubbing surfaces.

Earlier experiments in the macroscale as well as in the nanoscale showed that the three different oligomers of ethanolamine have different lubrication properties on 100Cr6 steel and copper [1], respectively. Ethanolamines act as multidentate ligands on the base of amino, hydroxyl and deprotonated hydroxyl groups of the total formula $NH_{3-n}R_n$ ($R = CH_2CH_2OH$, $n = 1–3$). Mono-, di- and triethanolamine are readily soluble in water and are utilized as additives in metalworking fluids. The understanding of the lubrication mechanisms of the additive layer chemisorbed on the specimens measured yields important information regarding lubrication optimization in term of the type of additive, type of isomer or oligomer and amount.

One of an unexplained mechanism is different lubrication properties of oligomers of ethanolamines. Whereas mono- and diethanolamine oligomer exhibit good lubrication properties triethanolamine oligomer do not and increase surface roughness by corrosive pit into the cooper surface.

To ensure the reliability of micro- and nano-devices as well as of magnetic storage devices, the application of lubricant film is required for the protection of the sliding surfaces from wear. Ideally, these films should be in the range of monomolecular layers because of small clearances in such devices and to minimize adhesion of sliding partners and to reduce wear and friction.

The classical approach to lubrication of micro- and nano-devices uses multi-molecular layers of liquid lubricants. Boundary films are formed by

- Physisorption: without exchange of electrons between the molecules of the adsorbate and adsorbent—this process involves weak Van der Waals forces.
- Chemisorption: where electrons shear and electron interchange between chemisorbed species and the solid surface by formation of covalent bonds.
- Chemical reaction: where films are formed by chemical reaction of the solid surface with the environment, the additive and the solid surface.

The stability and durability of the above surface films decrease in the following order: chemically reacted films (large film thickness), chemisorbed films (monomolecular layers) and physisorbed films (monomolecular to multimolecular layers).

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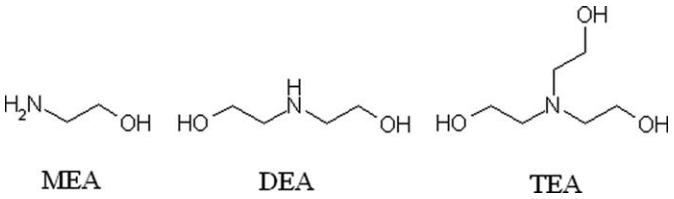

Fig. 1. Three oligomers of ethanolamine [1].

Sub-monomolecular films with a thickness in the order of a few nanometers, may be discontinuous and may deposit in an island form of non uniform thickness with lateral resolution in the nanometer scale [2].

A film fully covered with one layer of additive, often referred to as a monolayer, may reduce friction, wear, and rust, or may stabilize emulsions, foams, and solid dispersions.

In this study, we investigated so-called ethanolamines which have three different oligomers: monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA). The chemical structures are depicted in Fig. 1. Ehanolamines are multidentate ligands through amino, hydroxyl, and deprotonated hydroxyl groups, with the total formula $NH_{3-n}R_n$($R = CH_2CH_2OH$, $n = 1$–3).

Ethanolamines have a broad spectrum of applications, because they combine properties of amines and alcohols. Thus, they exhibit a unique capability of undergoing reactions common to both groups.

One not completely elucidated phenomenon concerns the different lubrication properties of oligomers of ethanolamines: Mono- and diethanolamine oligomer exhibit good lubrication properties whereas triethanolamine oligomer causes corrosive pits into the cooper surface.

In order to acquire knowledge of the tribological behavior of the oligomers at the interface between solids, a fundamental research work on the interaction of additive molecules with the surface is necessary.

XPS is the appropriate analytical method for the chemical analysis of adsorbents on surfaces. This technique is capable of characterizing the binding of the molecules to the surface as well as of providing concentration depth profiles of organic compounds adsorbed to solid surfaces. The chemical shift of the photoelectron peaks provides information about the atoms bound to the surface and is an indicator for the strength of the interaction between surface and additive. Angle resolved XPS is capable of determining the depth distribution of elements in each particular oxidation state in the first atomic layers. Moreover, the surface coverage can be deduced from the intensity dependent on the take-off angle of the photoelectrons. Finally, quantitative information about the composition can be gathered and quantitative concentration depth profiles are available [3].

2. Materials and methods

2.1. Sample preparation

Silicon wafers of $10 \times 10\,mm^2$ were cut from $5 \times 5\,cm^2$ sheets, and coated with 200 nm of copper by sputtering. The surface flatness of these coated slides was determined with an atomic force microscope (AFM MFP-3D, Asylum Research Santa Barbara, CA) in contact mode in air, and it turned out that the samples were almost flat at the atomic level.

Investigations by X-ray photoelectron spectroscopy (XPS) were performed using a VG ESCALAB Mk III equipment with a prototype preparation chamber permitting the transfer of samples from liquid to the analysis chamber under Helium protective gas preventing exposure to ambient conditions. The samples were transferred from the load lock chamber into the preparation chamber (5×10^{-9} mbar) of the XPS. It is well known that polluted sample surfaces change their properties [4]. For this reason, the specimens have been cleaned by argon ion sputtering until the XPS spectra of samples showed no peaks of contamination.

The 100Cr6 steel samples were prepared from sheets of $8 \times 12\,mm^2$, which were cut from roll from roller bearing. Then these samples were ground with abrasive paper down to 4000 μm, and then with DP-Spray P containing crystalline diamond with a grain size of 1 μm. The average roughnesses (RMS) of the samples were checked by AFM and gave values of approximately 20 nm.

2.2. Preparation of ethanolamine oligomer solutions

Each ethanolamine oligomer was dissolved in double distilled water to a concentration of 250 ppm. All water solutions had the same molar content (molecular concentration). Concentrations of the additives were significantly below saturation concentration, to prevent growth of additive crystals on the copper surface.

For the experiments, the solutions were then transferred into the electrochemical device consisting of two supply reservoirs, one was used as storage of double distilled water for rinsing the samples and the other contained the additive solution of the absorbents. A pressure line, which was filled with He 6.0 provided the pressure to transport the liquids into the adsorption vessel. In the adsorption vessel the samples were prepared. Bubblers were used to release the pressure and to keep air out of the system. Thus, the entire device was permanent under a slight overpressure of He. Furthermore, the He flow was used to flush the solutions in the storage supply in order to degas the solution [5].

The clean copper sheets were transferred from the preparation chamber of the XPS spectrometer directly into the adsorption vessel of the electrochemical device. There, they were dipped in 0.025% solutions of the adsorbates for 10 min at room temperature.

The clean copper sheets were transferred from the preparation chamber of the XPS directly into the adsorption vessel of the electrochemical device. There, they were dipped in 250 ppm solutions of the ethanolamines for 10 min at room temperature. Afterwards, the samples were rinsed with double distilled water, blown dry with He and transferred directly without exposing them to environment into the preparation chamber of the XPS [6].

2.3. Data acquisition

For XPS spectra, the samples were transferred from the preparation into the analysis chamber ($< 5 \times 10^{-10}$ mbar, except for sputtering). In angle resolved measurements (ARXPS), the angle between the sample surface and the analyzer, which is called emission angle, was altered by rotating the samples around the *x*-axis. This corresponded to rotations at angles of 0° and 80°. The emission angle was calculated from the geometric factors. Therefore, the emission angles calculated for the geometries used in the experiments were 15° and 70°.

All XPS measurements were performed using aluminum Kα radiation. The energy covered a range from 0 to 1400 eV binding energy. Spectra of C 1s, O 1s, N 1s and Cu 2p for silicon samples with copper layer and Fe 2p for steel samples were recorded.

2.4. Tribological experiments

The TOG tribometer, a translatorily oscillating test machine as shown in Fig. 2, was chosen for the investigation of lubricity on a macroscopic scale. TOG is widely used for the study of the

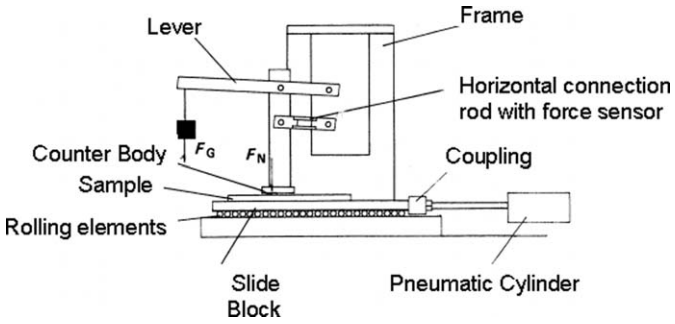

Fig. 2. Sketch of the TOG tribometer with the denotation of the parts described and used for the calculation of the coefficient of friction.

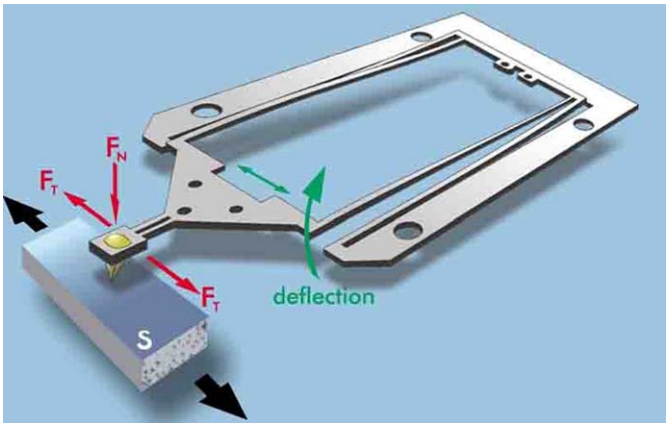

Fig. 3. Functional principle of the force transducer in microtribometer [7].

tribological behavior of tribo-partners with translatory relative movement to evaluate material combinations in a dry or wet lubrication regime.

The tribometer sample holder for testing in lubricants itself was screwed to a plate, which was fixed on the carriage. The carriage resides on a roller bearing and is driven by pneumatics. If the parallel lever system is adjusted in a way that the levers are parallel to the surface of the sample during tribotesting, friction force can be easily calculated from the stress measured by resistance strain gauge and the load applied and the dimensions of the tribometer.

2.5. Micro-tribometer FALEX-MUST 2D-FM

The tribometer FALEX-MUST 2D-FM working in reciprocating mode was used for copper sputtered silicon wafers to apply small loads from 1 mN to 1 N in order to prevent the silicon wafers from breaking. As counter body a steel ball mounted on a 2D force transducer was used. The normal force F_N (rectangular to the surface), the tangential force F_T (parallel to the surface of the test sample and opposing the relative velocity) and the moving way s were recorded over time t while the sample (copper coated silicon wafer) was moved in reciprocating mode.

Fig. 3 depicts the functional principle of this micro-tribometer. The FALEX-MUST 2D-FM special force transducer consists of a cantilever based on parallel spring system, two mirrors fixed on a moving part of the cantilever and a mechanical carrier. The cantilever is fixed on the mechanical carrier and helps to change the measurement mode of the force transducer. The two mirrors positioned orthogonally to each other are used as reflective surface for the fiber optic sensors (FOS). FOS is for the measurement of the deflection of the force transducer and the positioning of the piezo drives.

In the tribological experiments, the steel ball which was loaded against the copper coated silicon wafer. The chosen test parameters are listed in Table 1.

Table 1
Test parameters for copper coated silicon wafers sliding against steel balls in micro-tribometer FALEX-MUST 2D-FM.

Material	100Cr6 steel ball
Target force	30 mN
Stroke length	7 mm
Scan speed	5 mm/s
Number of cycles per track	10

3. Results

3.1. Micro-tribometer

The results obtained with micro-tribometer show that ethanolamine oligomers dissolved in water lower the friction at a concentration of 250 ppm. Monoethanolamine oligomer reduces friction by 63% and the friction coefficient in this case is the smallest. Diethanolamine reduce friction coefficient by 25% and triethanolamine by 44% (Fig. 4).

3.2. TOG

The TOG tribometer is based on a steel cylinder which is loaded against the steel sample. The sample was mounted on a special sample holder, which had been constructed for tribotesting in lubricants. During the measuring process the cylinder was oscillating in certain frequency and was in constant contact with the sample (see Fig. 2).

The 12 N load was applied to the upper specimen holder where the cylinder was mounted to press on a sample. For substances the test were carried only once.

The results show that ethanolamine oligomers dissolved in water lower the friction at a concentration of 250 ppm. Monoethanolamine and diethanolamine oligomer reduce friction the mostly by 58% and 37%, whereas triethanolamine only by 11%.

In previous work [1] the Atomic Force microscopy studies with nano-Newton resolution were performed with a MFP-3D from Asylum Research. Set point-applied load on the sample by cantilever was 3.3 nN. The results showed the same tribological behavior of ethanolamines as in macroscale, that the lowest friction coefficient was observed for monoethanolamine oligomer.

The differences in tribological behavior were observed by AFM with 3.3 nN load, microtribometer with 30 mN load and with TOG tribometer with 12 N load. Results show that monoethanolamine oligomer and diethanolamine oligomer have an excellent behavior regarding all tested parameters. Triethanolamine oligomer increases surface roughness by corrosive pit into the copper surface (Fig. 5).

3.3. XPS results

3.3.1. Copper surface

The survey spectra of all copper samples showed only peaks of copper, oxygen, nitrogen and carbon as expected. The position of photoelectron peaks was determined using Casa XPS, and a combination of Gaussian and Lorentzian peak was used for fit.

The adsorption of ethanolamine oligomers onto atomically flat surface of copper layer takes only 10 min. The survey spectra

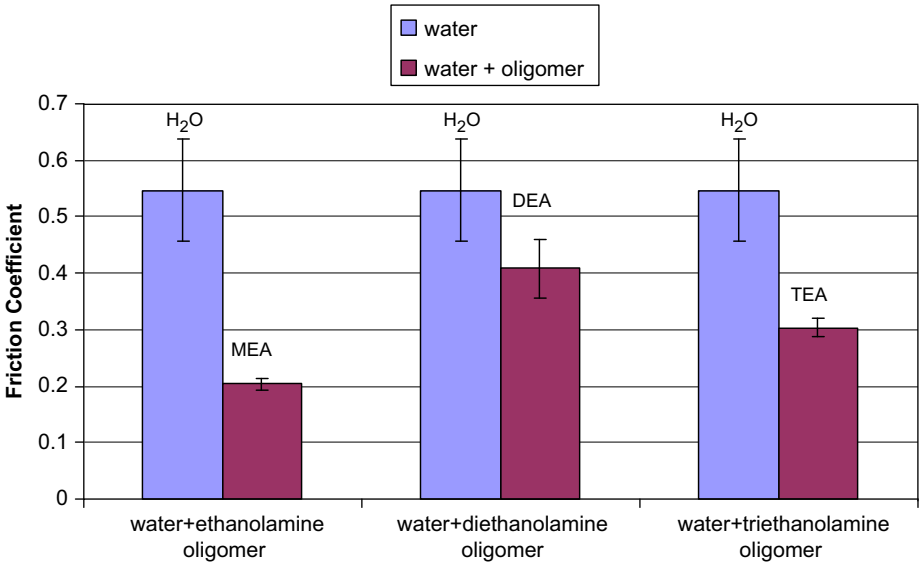

Fig. 4. Microtribometer results showing drop of friction coefficient for three oligomers of ethanolamines compare to double distilled water.

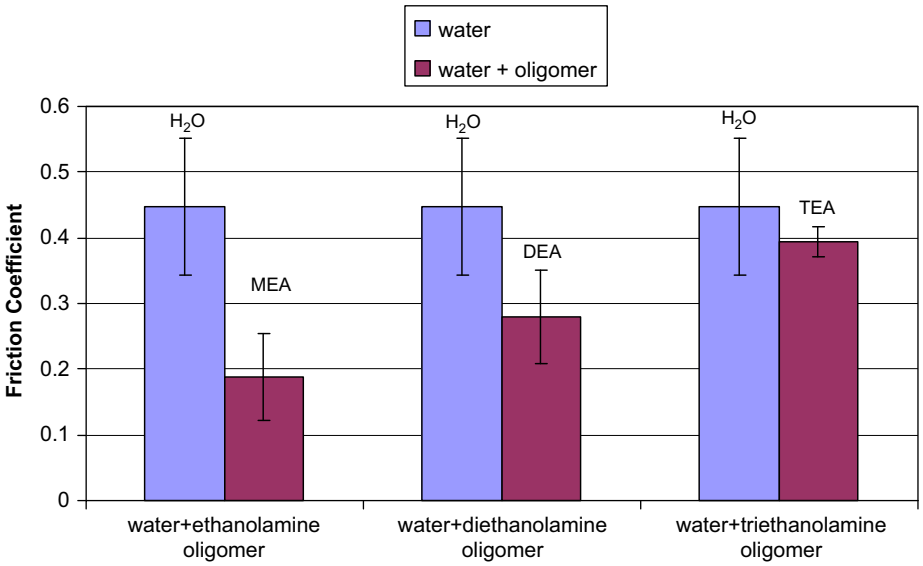

Fig. 5. TOG results showing drop of friction coefficient for three oligomers of ethanolamines compare to double distilled water.

shows that after this time surface adsorb a measurable amount of the oligomers.

The quantification of the O1s and C1s showed that there was an equal amount of both oxygen and carbon in the adsorbed films. The C1s peak was in the region typical for alcohols and organic compounds containing nitrogen.

The Cu 2p photoelectron region of diethanolamine showed different intensity ratio of the copper peak on clean surface and the copper peak with DEA film. The loss in intensity of iron peak was due to the coverage of the surface with the adsorbed diethanolamine. At emission angle 70° the Cu peak almost vanished in the spectra recorded from samples with diethanolamine film (Fig. 6).

First results obtained for diethanolamine present clearly the orientation of the molecules on the surface. The intensity of oxygen peak O1s and carbon peak C1s increase with increasing analyzer angle, and copper peak $2p_{1/2}$ and $2p_{3/2}$ and nitrogen N1s peak decreasing with emission angle (Fig. 7). This result indicates that oxygen and carbon was located on top, copper and nitrogen were beneath. Therefore it was deduced that the molecules stand upright on the surface, bound to it by the nitrogen atom. The intensity of copper continuously declines, therefore the whole surface is covered with molecules of diethanolamine.

In Fig. 7, can be clearly seen that the intensity of copper continuously declines, therefore the whole surface is covered with molecules of diethanolamine.

Angular resolved measurements showed that three oxygen species were situated in different heights. The one located on the top appear to increase with emission angle—this corresponds to oxygen from hydroxyl group (HO–CH_2 bonding). The depth distribution of the underlying one corresponds to copper oxide. The last to oxygen from water used to blow up sample after deposition monolayer.

3.3.2. *Steel surface*

For 100Cr6 steel sample with deposited diethanolamine oligomer monomolecular layer AR-XPS measurements showed slightly different behavior.

The Fe photoelectron region of diethanolamine showed a completely different intensity ratio of the iron and the iron oxide

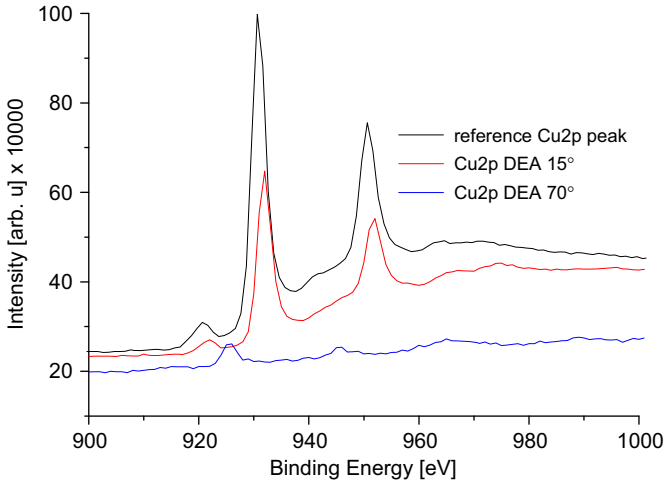

Fig. 6. Cu 2p region of monolayer of DEA on copper surface. The spectra are shown for two different electron take off angles. For comparison the spectra of clean copper are also shown.

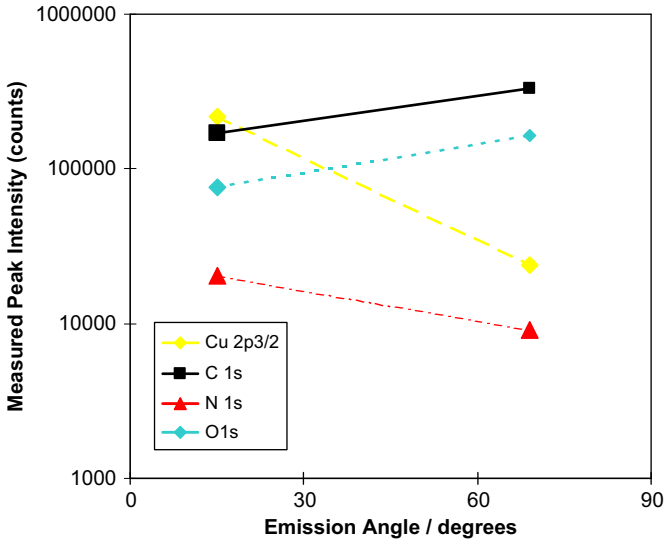

Fig. 7. Intensity ratios of diethanolamine oligomer XPS peaks depending on the take off angle (with the surface normal).

peak (Fig. 8). The loss in intensity of iron peak was due to the coverage of the surface with the chemisorbed diethanolamine oligomer film. At emission angle 63° the Fe metal peak almost vanished in the spectra recorded from samples with diethanolamine film.

Angular resolved measurements showed that Fe 2p peak contain three iron species situated in different heights (Fig. 9). The peak at 706.5 eV was attributed to pure iron, and the one at 710 eV to iron oxide [8,9]. Other peak at about 702.3 eV may result from Fe bond to nitrogen as assigned by Riviere and co-workers [10,11].

The C1s peak as well as the O1s peak consist of three peaks. The positions of O1s peaks are: 529.2 eV attributed to iron oxides [8,9], 531.6 eV to oxygen from water used as solvent [8], 525.6 eV to oxygen in hydroxyl group [12].

The N1s peak was found on both steel and copper samples after deposition DEA film. In both cases N1s peak consist of two species (Fig. 10).

On 100Cr6 steel surface positions of N1s peaks are 398.838 eV correspond to N bond to Fe [10,11], and 395.038 eV reported as NH–CH_2 [13]. Interesting is fact that with emission angle peak

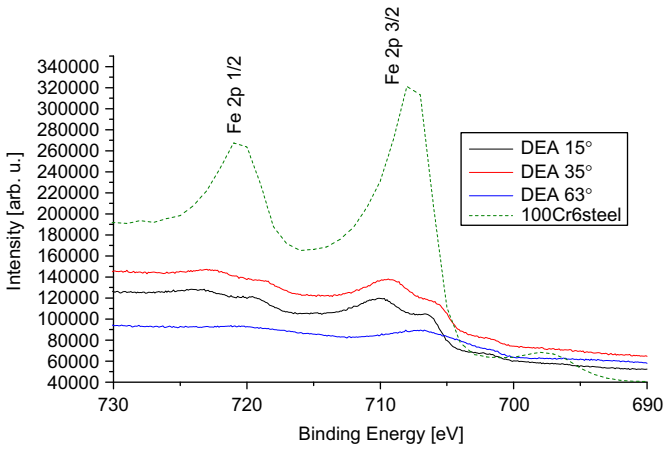

Fig. 8. Fe 2p region of monolayers of DEA on 100Cr6 steel. The spectra are shown for three different electron take off angles. For comparison the spectra of clean 100Cr6 steel is also shown.

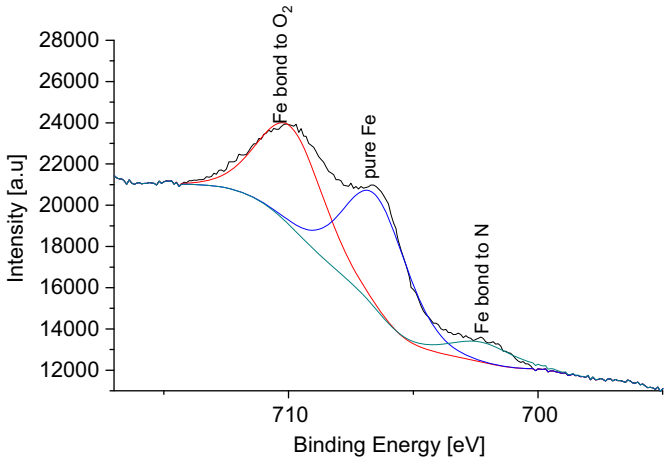

Fig. 9. Fe 2p region of monolayers of DEA on 100Cr6 steel with emission angle 15°.

intensity of NH–CH_2 increase, and N bond to Fe corresponding peak decrease as it is shown on Fig. 11.

In case of N1s on copper surface two composites also have been observed at binding energy: 402 eV correspond to as NH–CH_2 as it was observed for DEA molecules [13] and 396.1 eV, this peak could not be definitely assigned. It may be result from Cu bond to nitrogen, but there was no confirmation in Cu2p peak.

Detail analysis of angular resolved measurements of peaks Cu, Fe, O, C and N confirm our theory that the molecules of diethanolamine oligomer stand upright on the surface, bound to it by the nitrogen atom.

Multi point acquisition done with Auger Electron Spectroscopy and Scanning Electron Microscopy images confirm obtained results, showed that the whole surface is covered by homogenious layer of tribofilm, and Auger spectra showed C1s, N1s and O1s peaks which are the elements of ethanolamines.

In case of monoethanolamine and triethanolamine multi point acquisition performed with Auger Electron Spectroscopy and Scanning Electron Microscopy, the image shows that not a whole surface is covered by uniform layer of ethanolamine oligomer. Auger spectra in different positions showed different amounts of additives.

Additionally, depth profiles were recorded with Ar ions in Auger Electron Spectroscopy. For three cases of ethanolamine oligomers, the film created on the surface was very thin and was

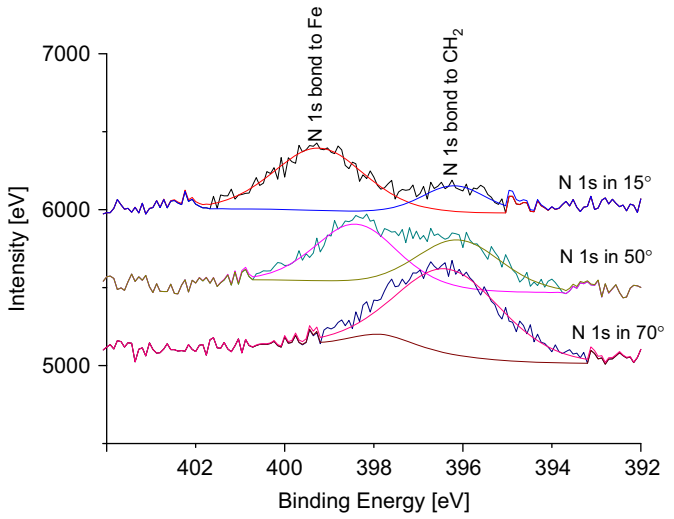

Fig. 10. N 1s region of monolayers of DEA on 100Cr6 steel. The spectra are shown for three different electron take off angles.

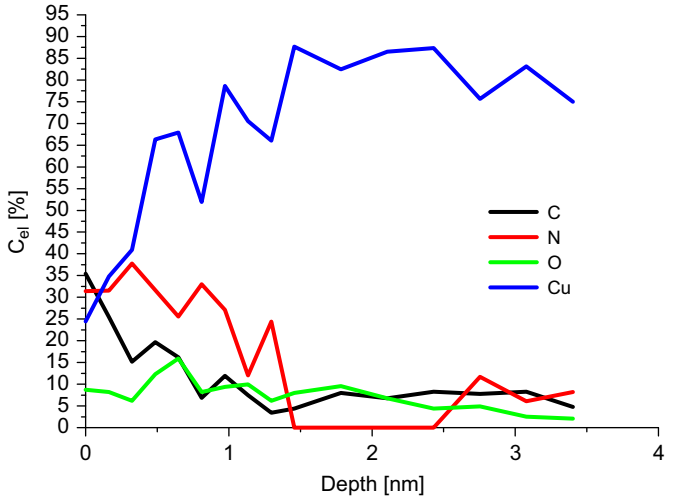

Fig. 11. Depth profile with Ar ions on AES.

between 1 and 2 nm. The nitrogen, carbon and oxygen peak was observed only in the first layer (see Fig. 11).

Future angle resolved XPS measurements on mono and triethanolamine on copper and steel surfaces are planned, to prove chemical bonding between copper with nitrogen and steel with nitrogen. Future studies are needed to check chemisorption of ethanolamine oligomers on other surfaces.

4. Discussion, conclusion and outlook

In this paper, oligomer specific lubrication was studied. Differences in tribological behavior of the oligomers of ethanolamine have been observed by AFM, microtribometer and TOG tribometer and the chemical structure of the film by XPS.

Very interesting is the fact that the same behavior of the friction coefficient is observed for a wide range of loads, from the nano- to the micro and macro range.

The obtained results show that the additives undergo reactions during adsorption, and it takes only 10 min for the film to strongly adhere to the substrate.

The lowest friction coefficient is observed for monoethanolamine oligomer, for di- and tri-ethanolamines the friction coefficient was higher. The results show that differences in tribological behavior might be due to the orientation of hydroxyl groups on the surface.

Detail analysis of angular resolved measurements of peaks Cu, Fe, O, C and N showed that the molecules of diethanolamine oligomer stand upright on the surface, bound to it by the nitrogen atom. Number of hydroxyl groups in chemical compound have influence friction behavior.

More detailed studies with all ethanolamines on steel and other surfaces shall be undertaken. Further detailed studies are necessary to link macrotribological results with information on structural chemistry obtained by XPS.

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