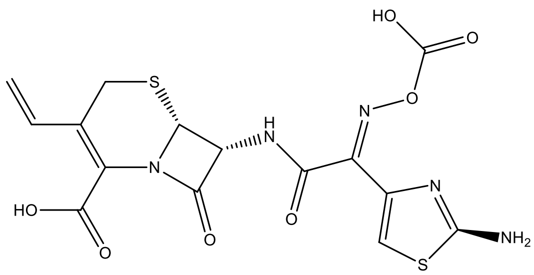
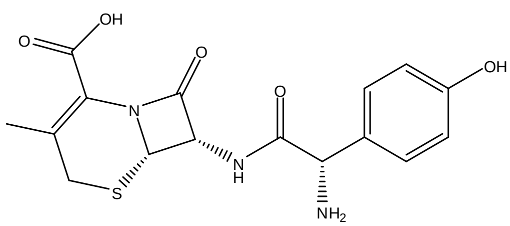
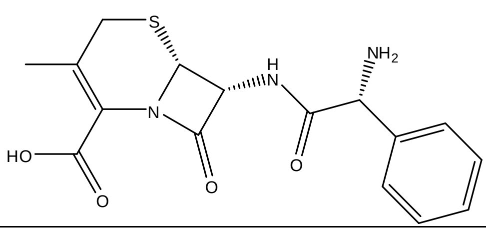
The present chapter reports investigations on studies of non-toxic and eco-friendly heterocyclic *β*-lactam antibiotics like cefixime, cefadroxil and cephalexin as new ashless low SAPS antiwear additives in neutral paraffinic base oil under boundary lubrication conditions. The chemical film formed on interacting metallic surfaces during sliding conditions has been characterized by X-ray photoelectron spectroscopy (XPS), and its elemental composition has been determined by energy dispersive spectroscopy (EDS). Surface morphology and roughness of the worn surface have been examined using scanning electron microscopy (SEM) and contact mode atomic force microscopy (AFM), respectively. Quantum chemical calculations based on density functional theory (DFT) have been performed to correlate their antiwear properties with the structures. The obtained experimental results have been found to be in good agreement with the theoretical calculations using DFT.

## 3.1. Materials & methods

### 3.1.1. Chemicals

All of the chemicals and solvents were obtained from commercial sources and used as supplied. The solvent *n*-hexane used for cleaning the specimen was obtained from Fisher Scientific Co. (Mumbai, India). Zinc dibutyldithiophosphate (ZDDP) was procured from Flexsys Chemicals (M) SdnBhd, U.S.A. and used as reference additive. The *β*-lactum antibiotics cefixime from Schwitz Biotech, Ahmedabad, India; cefadroxil and cephalexin from Orchid Chemicals & Pharmaceuticals Limited, Chennai, India were used in the investigation. Chemical structures and IUPAC names of the tested antibiotics are listed in Table 3.1. These were used without further purification.

**Table 3.1.** Molecular structure and commercial name of investigated $\beta$-lactum antiwear lubricant additives

| Structure | IUPAC Name | Commercial Name |
|---|---|---|
|  | (6R,7R)-7-((E)-2-((R)-2-amino-2,3-dihydrothiazole-4yl)-2-(corboxyimino)acetamido)-8-oxo-3-vinyl-5-thia-1-azabicyclo [4,2,0]oct-2-ene-corboxylic acid | Cefixime |
|  | (6S,7S)-7-((S)-2-amino-2-(4-hydroxyphenyl)acetamido)-3-methyl-8-oxo-5-thia-1-azabicyclo [4,2,0]oct-2-ene-corboxylic acid | Cefadroxil |
|  | (6R,7R)-7-((R)-2-amino-2-phenylacetamido)-3-methyl-8-oxo-5-thia-1-azabicyclo[4,2,0] oct-2-ene-corboxylic acid | Cephalexin |

## 3.2. Tribological Characterization

### 3.2.1. Lubricant Sample Preparation

Paraffin oil blends (uniform solution/suspension) with various concentrations of different $\beta$-lactum antibiotics as additives from 0.5 to 1.5% (w/v) were made by stirring for 1-2h on magnetic stirrer. The entire antiwear and load carrying tests were carried out at an optimized concentration 1.0% (w/v) of antiwear additives and compared with those of 1.0 % (w/v) ZDDP.

## 3.3. Results and discussion

### 3.3.1 Antiwear properties

The mean wear scar diameter (MWD) is an indication of extent of wear when sliding contacts occurs. The concentration of $\beta$-lactum antibiotics was optimized by varying it from 0.5 to 1.5% w/v and measuring the corresponding MWD at 392N applied load for 60 min. test duration. Figure 3.1 exhibits the optimization results of $\beta$-lactum antibiotics showing variation of MWD with change in concentrations of the additives from 0.5 to 1.5% (w/v). It can be clearly seen that the value of MWD dramatically decreases for all the additives when their concentration is increased from 0.5 to 1.5% (w/v). Thus the additives improve the antiwear properties of paraffin oil at all the tested concentrations. The observed MWD values for all the additives are found to be the lowest at 1.0% w/v concentration. The cefixime shows maximum decrease in MWD at all the concentrations followed by cefadroxil and cephalexin. As distinct from the figure, beyond the optimum concentration of additives the MWD is almost constant. Therefore, entire antiwear tests were carried out at 1% w/v which is the optimized concentration of the additives.

Figure 3.2 shows variation of MWD in the presence of all the tested antiwear additives, $\beta$-lactum antibiotics and zinc dibutyldithiophosphate (ZDDP) in paraffin oil at the applied load 392N for 60 min test duration. It is apparent from the figure that the largest MWD (0.681mm) was observed in case of pure paraffin oil while it was the smallest in presence of cefixime (0.524mm). Addition of additives to the base oil significantly reduces the value of wear scar diameter. All the $\beta$-lactum antibiotics reduce the MWD much more than the high SAPS containing conventional ZDDP. This is attributed to the fact that the investigated additives are polar molecules with a number of active centers which facilitate their adsorption on steel surface. Among all $\beta$-lactum antibiotics, cefixime exhibits excellent antiwear properties.

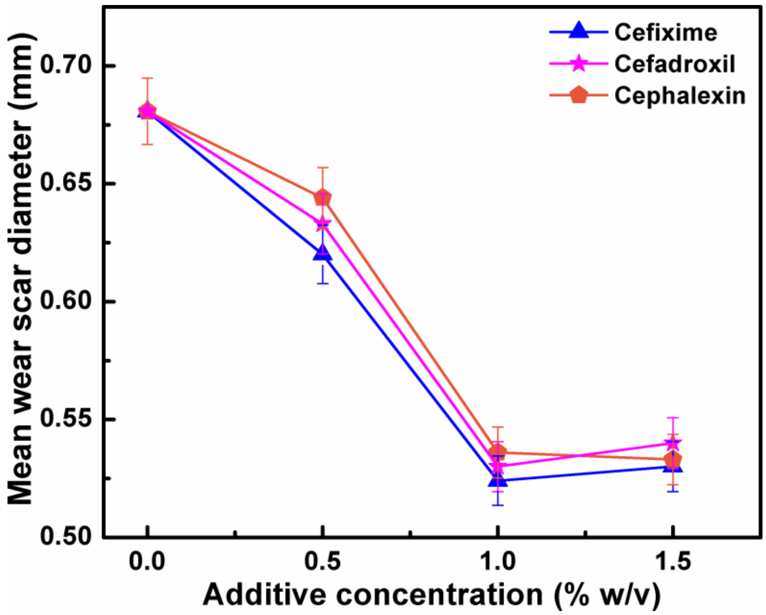



**Figure 3.1.** Variation of mean wear scar diameter in absence and presence of different concentrations of $\beta$-lactum additives in paraffin oil at 392N applied load and 60 min. duration

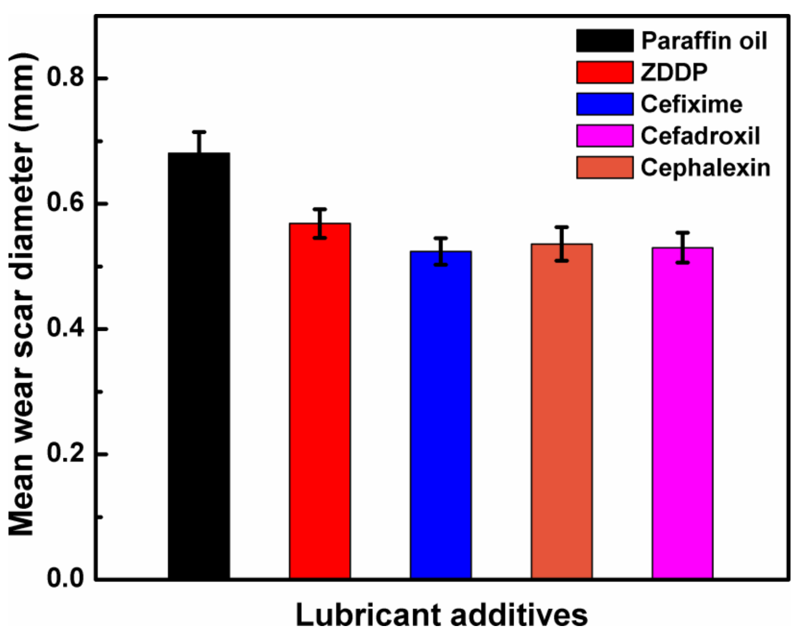



**Figure 3.2.** Variation of mean wear scar diameter in paraffin oil with and without different antiwear additives (1% w/v) at 392N applied load for 60 min. test duration

In order to investigate the effect of sliding time on the mean wear scar diameter, the antiwear tests have been also carried out at 392N applied load for different time durations, 15, 30, 45, 60, 75 and 90 min for paraffin oil in presence and absence of antiwear additives. The variation of MWD with respect to time durations at 392N load is represented in Figure 3.3 and the obtained results are collected in Table 3.2. It is evident from the Figure 3.3 that the MWD in case of paraffin oil for all the test durations is found to be much larger than in the presence of additives. Initially, for 15 min of test duration, the MWD in the presence of $\beta$-lactum additives is nearly the same but it is much smaller in case of ZDDP. After that further increase in test duration up to 30 min, there is abrupt increase in MWD for ZDDP whereas its value increases quite smoothly for $\beta$-lactum additives. Although the activity of different $\beta$-lactum antibiotics could not be differentiated for 15 min test duration, these can be well differentiated at 30 min test run and thereafter. The blends with cefixime and cefadroxil additives show comparatively much smaller MWD than ZDDP indicating better adsorption of these additives on steel surface. On the other hand, in case of cephadroxil MWD observed is larger than that in presence of ZDDP. The value of MWD for cefixime was found to be the lowest for all test durations from 30-90 min.

It is apparent from the Figure 3.3 that initially up to 30 min, the rate of increase in MWD is greater for paraffin oil in presence and absence of additives but later on up to 90 min, it slightly decreases and increases linearly with increase in time duration for all the additives. Further, there is sudden increase in the value of MWD at 90 min test run in case of paraffin oil alone, however, in presence of additives a gradual increase in MWD is observed.

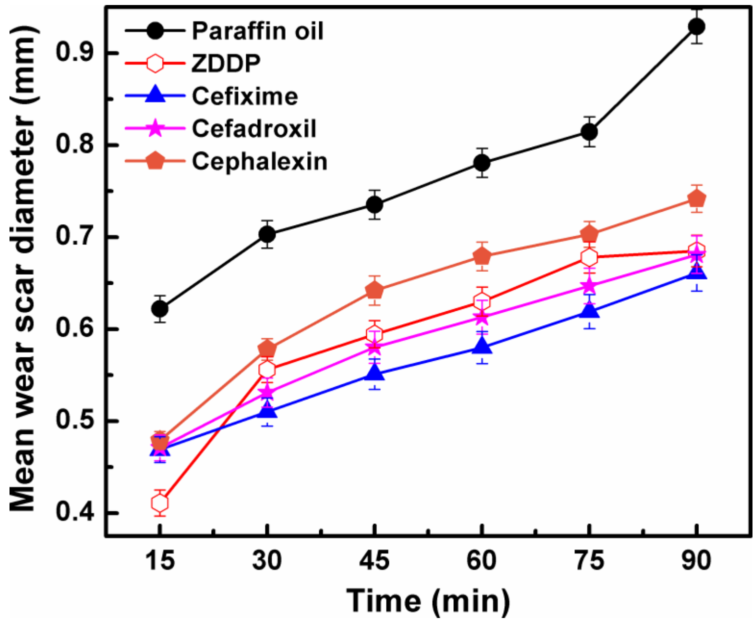



**Figure 3.3.** Variation of mean wear scar diameter with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate and $\beta$-lactum additives at 392N applied load

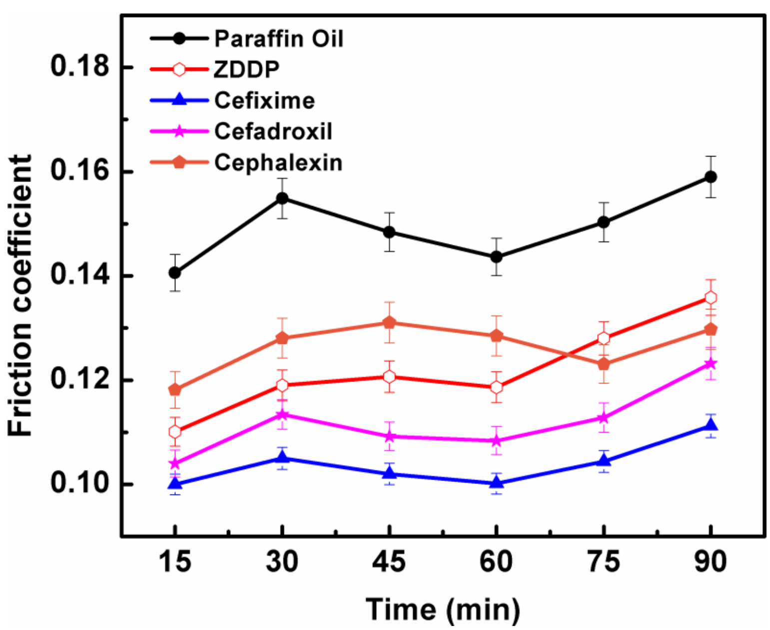



**Figure 3.4.** Variation of friction coefficient with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate and $\beta$-lactum additives at 392N applied load

**Table 3.2.** Tribological parameters for paraffin oil in the presence and absence of $\beta$-lactum antiwear additives (1% w/v) for different time durations at 392N applied load

| S.N. | Additive | Time (min) 15 | | 30 | | 45 | | 60 | | 75 | | 90 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | MWD (mm) | MWV ($10^{-4}$ $mm^3$) | MWD (mm) | MWV ($10^{-4}$ $mm^3$) | MWD (mm) | MWV ($10^{-4}$ $mm^3$) | MWD (mm) | MWV ($10^{-4}$ $mm^3$) | MWD (mm) | MWV ($10^{-4}$ $mm^3$) | MWD (mm) | MWV ($10^{-4}$ $mm^3$) |
| 1. | Paraffin oil | 0.622 | 20.548 | 0.703 | 34.829 | 0.735 | 42.152 | 0.781 | 54.177 | 0.815 | 64.647 | 0.929 | 111.280 |
| 2. | ZDDP | 0.411 | 02.698 | 0.556 | 12.457 | 0.594 | 16.821 | 0.630 | 21.728 | 0.678 | 29.843 | 0.685 | 31.184 |
| 3. | Cefixime | 0.469 | 05.525 | 0.510 | 08.333 | 0.551 | 11.924 | 0.580 | 15.078 | 0.619 | 20.117 | 0.661 | 26.758 |
| 4. | Cephalexin | 0.479 | 06.143 | 0.578 | 14.846 | 0.642 | 23.587 | 0.679 | 30.032 | 0.703 | 34.829 | 0.742 | 43.695 |
| 5. | Cefadroxil | 0.471 | 05.645 | 0.531 | 10.078 | 0.581 | 15.113 | 0.613 | 19.275 | 0.647 | 24.394 | 0.681 | 30.412 |

MWD= Mean wear scar diameter, MWV = Mean wear volume

This may be due to the fact that initially there is no tribofilm on the interacting surfaces. As the time increases the additive molecules get decomposed during sliding under operating conditions (high load and high temperature) and reacted with metal surface to form tribochemical film. The formation of tribofilm is time dependent; therefore, time exposure is required to form a durable tribofilm on sliding surfaces **[**Cavdar *et al.*(1991)]. The excellent antiwear behavior is shown by the cefixime since it contains greater number of active centers through which it may be adsorbed on the metal surface. It might be one of the reasons behind the observed trend of additives in the present investigation.

Figure 3.4 illustrates the variation of friction coefficient with time in absence and presence of 1% w/v ZDDP/$\beta$-lactum antibiotics in paraffin oil for 392N applied load. It can be seen that the admixture of base oil with cefixime and cefadroxil gives the lower friction coefficient than that with ZDDP or cephalexin. For ZDDP and cephalexin friction coefficient increases initially up to 45 min test run and then it slightly decreases or remains constant up to 75 min duration whereas cefixime and cefadroxil stabilize it earlier at 30 min test run. In every case, it has been observed that the value of friction coefficient starts shooting from 75-90 min duration. This may be due to the wear assisted surface damage and generation of wear debris produced with time under operating conditions at the interface. The friction coefficient data support the order of efficiency for different additives as discussed above, accordingly the highest friction coefficient for every run is observed for plain paraffin oil and the lowest for cefixime.

On the basis of variation of mean wear scar diameter and friction coefficient with time the order of antiwear efficiency is given below:

Cefixime > Cefadroxil > ZDDP > Cephalexin > Paraffin oil

To estimate wear more realistically it is important to examine the variation of mean wear volume with time instead of variation of mean wear scar diameter with time. According to equation 2.3, MWV contains MWD to the fourth power. Therefore, little change in the dimension of MWD causes huge changes in the MWV. Mean wear volumes in absence and presence of different additives at 392N load for paraffin oil were plotted with a function of time and a linear regression model was fitted on the points including origin to find overall wear rate, Figure 3.5. Overall wear rate was found to be very high in absence of additives. Among various $\beta$-lactum additives, the following order emerged for overall wear rate:-

Cefixime < Cefadroxil < Cephalexin

This again is in conformity with the conclusion drawn earlier that cefixime gets most strongly adsorbed on metal surface to form most adherent tribofilm and thus reducing wear to the greatest extent.

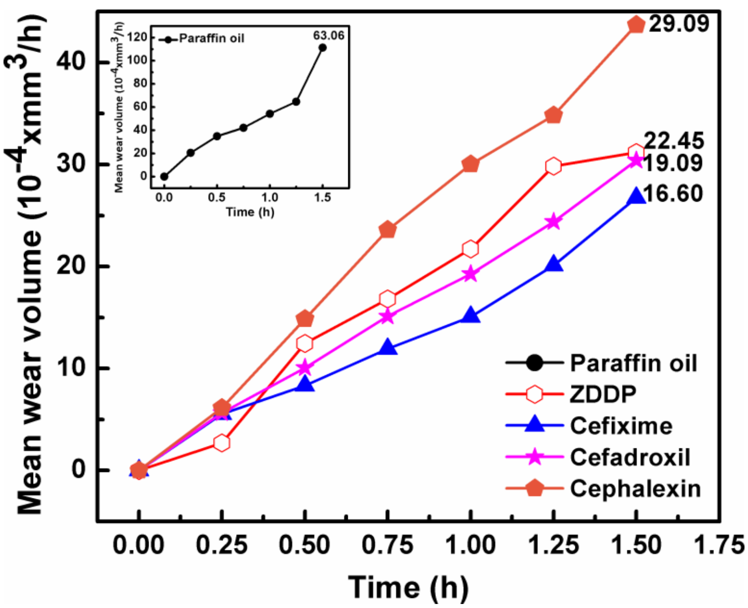



**Figure 3.5.** Determination of overall wear rate by varying mean wear volume with time (h) in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate and $\beta$-lactum additives at 392N applied load

Since running-in process refers to the adjustment of the surfaces moving under controlled conditions, the running-in wear rate is always higher than the steady-state wear rate. The values of overall, running-in and steady-state wear rates are listed in Table 3.3. Table 3.3 shows that the running-in wear rate is found to be much lower in case of cefixime and cefadroxil than ZDDP while the steady-state wear rates in their presence are comparable to ZDDP. The running-in and steady-state wear rates for paraffin oil in absence and presence of additives at 392N load have been mentioned in Figure 3.6 and Figure 3.7 respectively. The addition of antiwear lubricant additives to the paraffin base oil effectively reduces the overall, running-in and steady-state wear rates. Moreover, the steady-state wear rate is directly related to the machine life. Thus, for a better antiwear additive it is important to achieve steady-state as early as possible and it must be stable for longer duration. This behavior is evident with the additives cefixime, cefadroxil and ZDDP.

**Table 3.3.** Wear rates of paraffin oil in absence and presence of *β*-lactum antiwear additives at 392N applied load for 90 min test duration

| S.N. | Additives | Wear Rate($10^{-4}$x $mm^3$/h) | | |
|---|---|---|---|---|
| | | **Running-in** | **Steady-state** | **Overall** |
| 1. | Paraffin oil | 69.99 | 38.70 | 63.06 |
| 2. | ZDDP | 24.92 | 18.52 | 22.45 |
| 3. | Cefixime | 16.66 | 13.49 | 16.60 |
| 4. | Cefadroxil | 20.16 | 18.39 | 19.09 |
| 5. | Cephalexin | 32.70 | 29.36 | 29.09 |

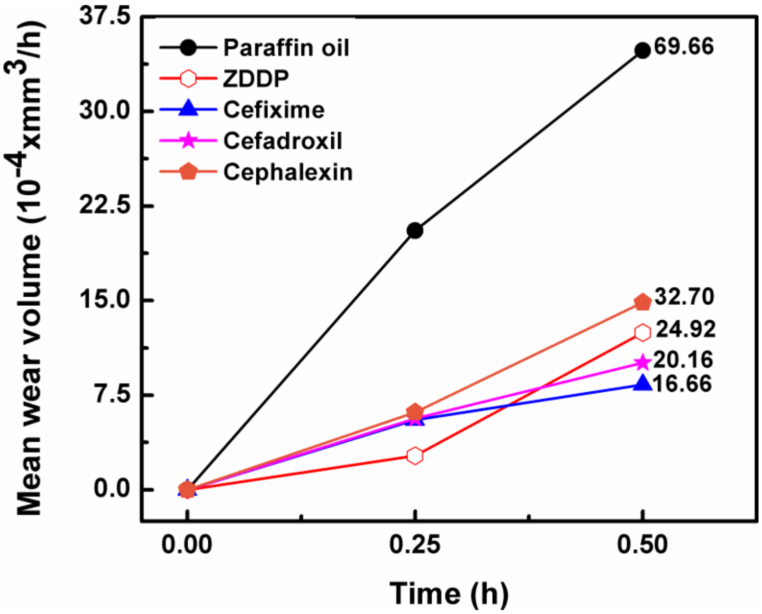



**Figure 3.6.** Determination of running-in wear rate by varying mean wear volume with time (h) in paraffin oil containing (1%w/v) zinc dibutyldithiophosphate and $\beta$-lactum additives at 392N applied load

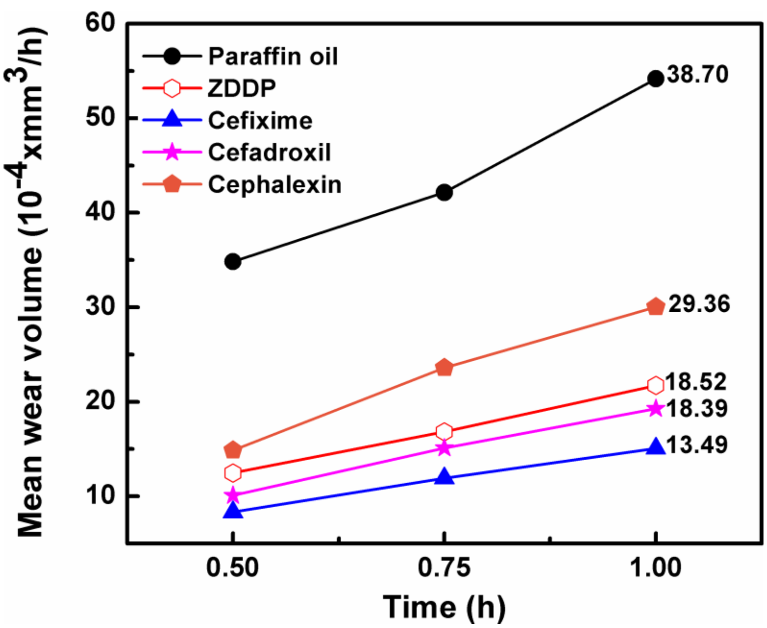



**Figure 3.7.** Determination of steady-state wear rate by varying mean wear volume with time (h) in paraffin oil containing (1%w/v) zinc dibutyldithiophosphate and $\beta$-lactum additives at 392N applied load

### 3.3.2. Effect of load

In order to investigate the effect of applied load on the mean wear scar diameter, the tests have been carried out at different loads 294, 392, 490, 588, 686 and 784N for 30 min test duration for paraffin oil in presence and absence of antiwear additives (1% w/v). Figure 3.8 represents plots of MWD as a function of applied load at 30 min test duration. It can be clearly shown from the figure that paraffin oil, ZDDP could sustain the load up to only 490 and 588N respectively whereas $\beta$-lactum additives reflect appreciable load carrying ability up to 784N.

At initial load (294N), MWD is very large in the absence of additives but in presence of $\beta$-lactum additives it is fairly reduced. With increase in load, at 392N MWD increases appreciably in every case but this increase is maximum in absence of additives. This shows that the thin film of lubricant and additive adsorbed on the interacting surfaces resists much increase in MWD on increasing applied load. At 490N load the base oil shows abrupt increase in MWD; however, the increase is very small in presence of the additives. This can be attributed to the formation of tribofilm in presence of additives. Thus, the tribofilm formed is further capable of carrying higher load. Beyond 490N load the tribofilm fails to sustain the load in case of paraffin oil while the film fails at 588N load in case of blends with ZDDP. On further increase in the applied load cephalexin could sustain the load up to 686N, cefadroxil somehow bears load up to 784N with large MWD but cefixime could successfully bear the load up to 784N without surface destruction. A comparison of MWD shows that its value in presence of cefixime at 784N is much lower than ZDDP at 588N indicating higher load carrying capacity of cefixime. This is one of the most striking feature of the investigated $\beta$-lactum additives.

Overall order of efficiency of $\beta$-lactum additives at every load was observed as:

Cefixime > Cefadroxil > Cephalexin> ZDDP> Paraffin oil

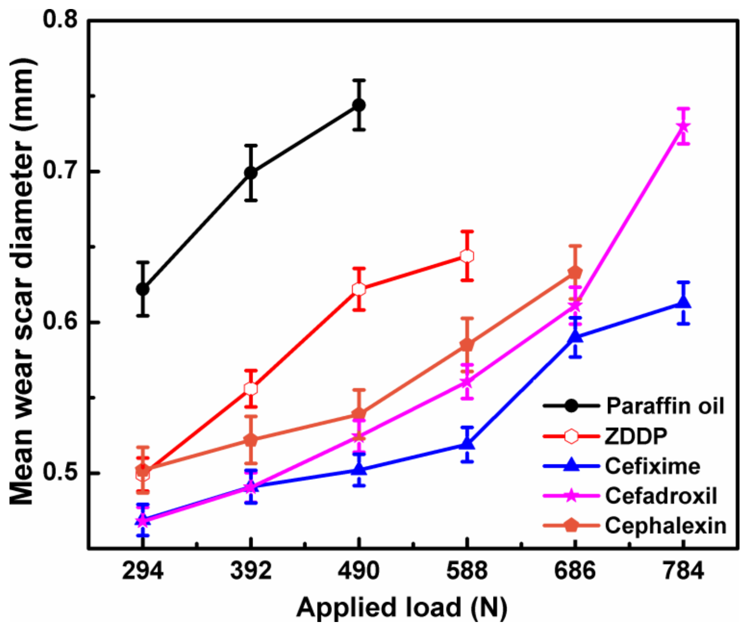



**Figure 3.8.** Variation of mean wear scar diameter with applied load in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate and $\beta$-lactum additives for 30 min. test duration

### 3.3.3. Surface Characterization

#### 3.3.3.1. Surface morphology

The topography of the wear scar surface has been studied by scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM). The SEM micrographs of the wear scar in the presence and absence of 1% w/v ZDDP, $\beta$-lactum additives tested at 392N load for 90 min test run are shown in Figure 3.9. A comparison of the SEM-images for paraffin oil alone and with additives, show that the surface is much more damaged in the former case (Figure 3.9a) while it is much smoother in the latter case (Figure 3.9b-e). Therefore, the new additives possess more significant antiwear properties than ZDDP. The extent of smoothening of worn surfaces has been found to be maximum in case of cefixime as it is evident from Figure 3.9c in which smaller grooves are seen. Besides this, the clear boundary of wear scar is also seen in inset. However, this extent of smoothening is found to be comparatively lesser in case of cefadroxil, cephalexin and ZDDP respectively. The observed smoothness of micrographs in presence of new additives follows the same order as inferred on the basis of their antiwear behavior discussed above. This smoothness of the surface may be correlated well with the observed order of running-in wear rate data:

Paraffin oil > Cephalexin > Cefadroxil > Cefixime

To investigate and compare the morphology of worn steel surfaces lubricated with cefixime and ZDDP at comparatively higher load, the SEM micrographs have been also taken at 588 N load for 30 min test duration. These micrographs are presented in Figure 3.10. It can be seen that the there is much more destruction of surface in case of ZDDP (Figure 3.10b), on the contrary, relatively much smoother surface has been obtained when cefixime (Figure 3.10a) is used.

Surface topography of the wear scars on the steel balls observed after antiwear tests in paraffin oil were examined by contact mode Atomic Force Microscopy in the presence and absence of the $\beta$-lactum antibiotics and ZDDP at 392N load for 90 min test duration. The *3D*-AFM images of the wear scar are shown in Figure 3.11. From the *3D*-AFM images, it is evident that there are huge differences in the average peak-valley height in case of surface lubricated with paraffin alone. However, in the presence of additives this difference is extremely small. The value of area roughness has been found to be maximum, 409 nm (Sq) for the base oil. The maximum reduction of surface roughness has been observed in case of cefixime (Sq= 57 nm) which indeed is much better than that in case of ZDDP (Sq=75 nm) under similar conditions. As apparent from the figures, the roughness has fairly reduced in the presence of additives. The addition of $\beta$-lactum antibiotics to the base oil drastically reduces the surface roughness. The reduction in surface roughness may be attributed to the tribofilm formed under test conditions by the adsorbed additive.

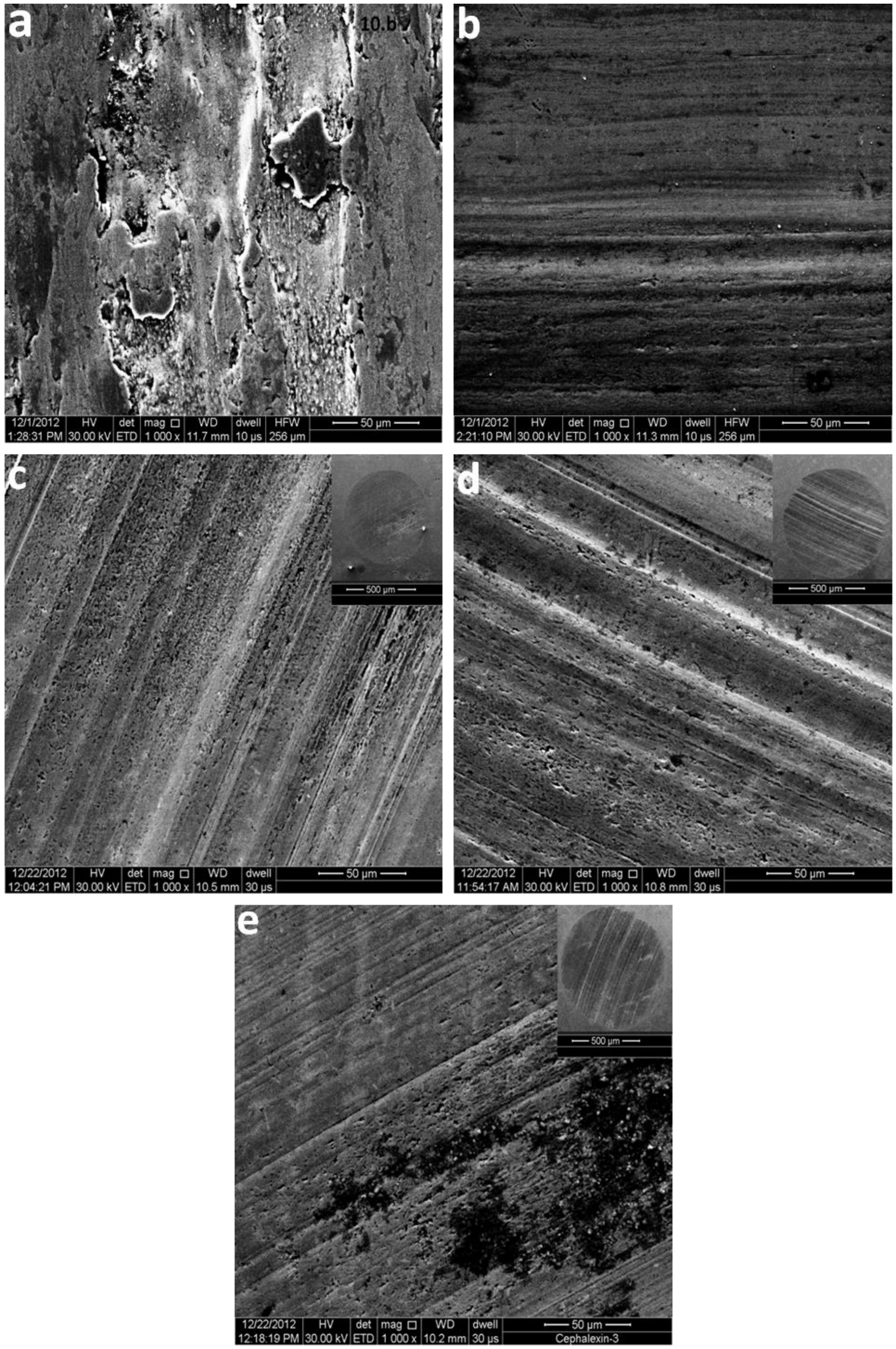



**Figure 3.9.** SEM micrographs at different magnifications of the worn steel surface lubricated with $\beta$-lactum additives (1% w/v) in paraffin oil for 90 min. test duration at 392 N applied load: (a) Paraffin oil, (b) ZDDP, (c) Cefixime, (d) Cefadroxil and (e) Cephalexin

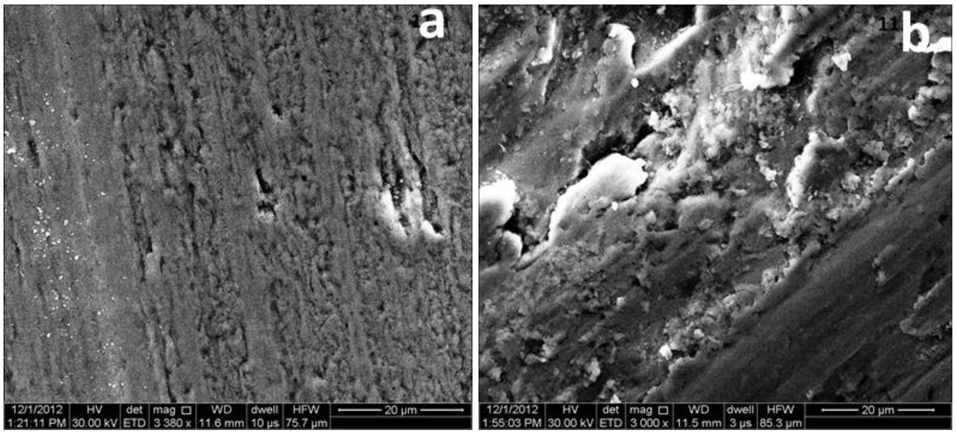



**Figure 3.10.** SEM micrographs of the worn steel surface lubricated with, (a) cefixime and (b) ZDDP (1% w/v) in paraffin oil for 30 min test duration at 588 N applied load

#### 3.3.3.2. Chemical analysis of tribofilm

The EDX spectra of the worn surface lubricated with paraffin oil, admixtures with ZDDP and cefixime have been recorded to determine the elemental compositions of the tribofilm at 392N load for 90 min test duration and are mentioned in Figure 3.12. The EDX spectrum of the worn steel surface lubricated with paraffin oil alone shows absence of additional peaks due to hetero atoms except oxygen which may be due to the oxide formation (Figure 3.12a). On the other hand, Figure 3.12b shows prominent additional peaks for zinc, phosphorous, sulfur and nitrogen on the wear scar surface lubricated with additive ZDDP. Herein, the best antiwear behavior shown by cefixime is due to the presence of sulfur and nitrogen in the EDX spectra (Figure 3.12c) of worn surface which reflects strong additive-metal interaction through which adsorption is facilitated. This brings about its tribochemical reaction with metal surface to form stable protective layers reducing friction and wear.

Besides this, to understand the tribochemical interaction of cefixime additive, the EDX spectrum (Figure 3.13) was also taken at a higher load, 588N, for 30 min duration. Figure 3.13 clearly depicts that the atomic concentration of hetero-atoms i.e. sulfur and nitrogen increases appreciably with increase in load which may be responsible for its high load-carrying capacity.

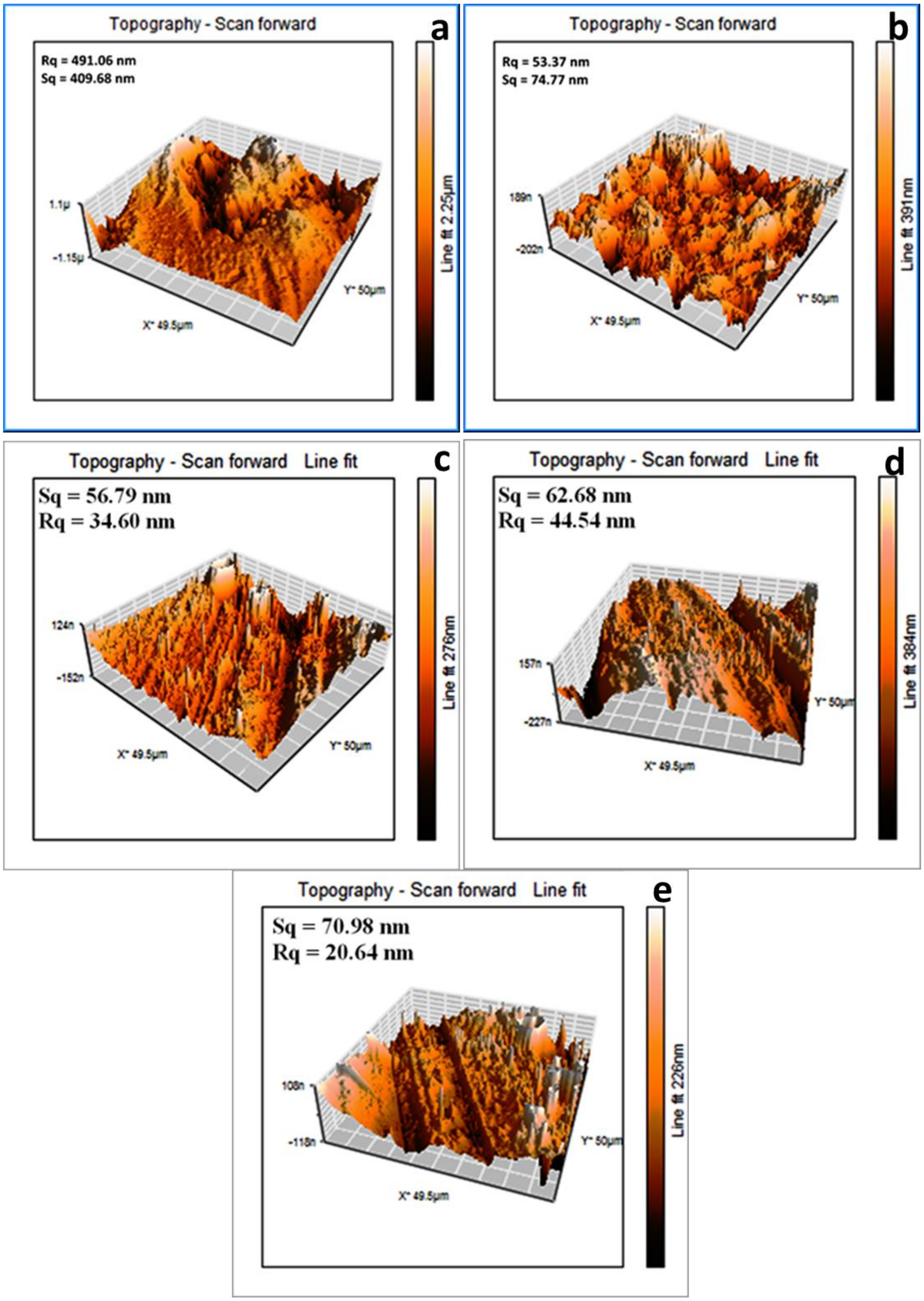



**Figure 3.11.** 3*D*-AFM images of the worn steel surface lubricated with $\beta$-lactum additives (1% w/v) in paraffin oil for 90 min test duration at 392 N applied load: (a) Paraffin oil, (b) Zinc dibutyldithiophosphate, (c) Cefixime, (d) Cefadroxil and (e) Cephalexin

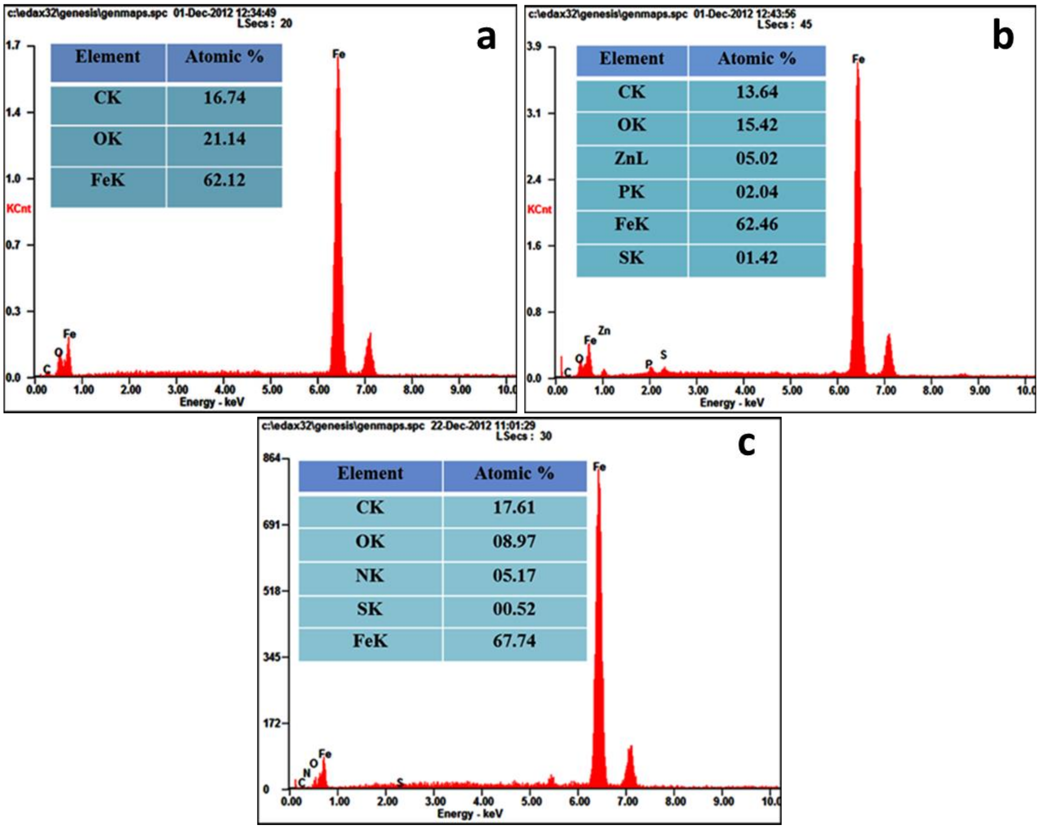



**Figure 3.12.** EDX analysis data of the worn steel surface lubricated with paraffin oil in presence and absence of additives (1% w/v) for 90 min test duration at 392 N applied load: (a) Paraffin oil, (b) Zinc dibutyldithiophosphate (ZDDP) and (c) Cefixime

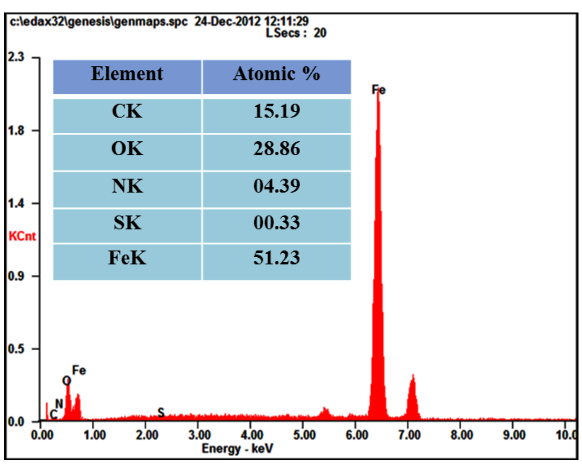



**Figure 3.13.** EDX analysis data of the worn steel surface lubricated with paraffin oil in presence cefixime additive (1% w/v) for 30 min test duration at 588 N applied load

The detailed chemical analysis of these chemisorbed elements on worn surfaces has been studied using XPS. The tribofilms generated on steel surfaces in presence of admixtures at various temperatures show that the additives undergo decomposition at much lower temperature than their normal decomposition temperature [Fuller *et al.*(1997)]. Thus, in order to ascertain the tribochemistry, XPS analysis of the worn scar in presence of the blend with cefixime at 392N load for 90 min test duration was carried out. Figure 3.14(a-e) shows the XPS spectra of C 1s, N 1s, S 2p, O 1s and Fe 2p of the wear scar. The spectrum of C 1s on the worn surface exhibits peaks at 285.0 and 289.0 eV corresponding to -C(O)O-and C-C/C-H moieties respectively [Singh *et al.*(2011)]. The binding energy of N 1s is about 399.9 eV which corresponds to the adsorbed nitrogen in the form of -N=C- and/or amide moiety [Wu *et al.*(2009)]. These moieties are also present in the molecular structure of cefixime which shows that these are the favorable sites for chemisorption on metal surfaces during sliding process. The spectrum of S 2p on worn surface illustrates the existence of peak at 168.5 eV showing occurrence of tribochemical reaction. On combining the S 2p peak with binding energy 532.2 eV of O 1s spectra, it can be further ascertained that there must be *in situ* formation of $FeSO_4$ during tribochemical reaction [Zeng *et al.*(2007)]. Further, in case of oxygen another peak of O 1s is also observed at binding energy of 530.2 eV corresponding to its chemical state in the tribochemical species $Fe_3O_4$ and/or $Fe_2O_3$. Combining the binding energies of O 1s at 530.2 eV with Fe 2p at 710.9 eV, it can be stated that iron has oxidized to $Fe_2O_3$ and $Fe_3O_4$ during rubbing process [Zhou *et al.*(2001) and Li *et al.*(2010)].

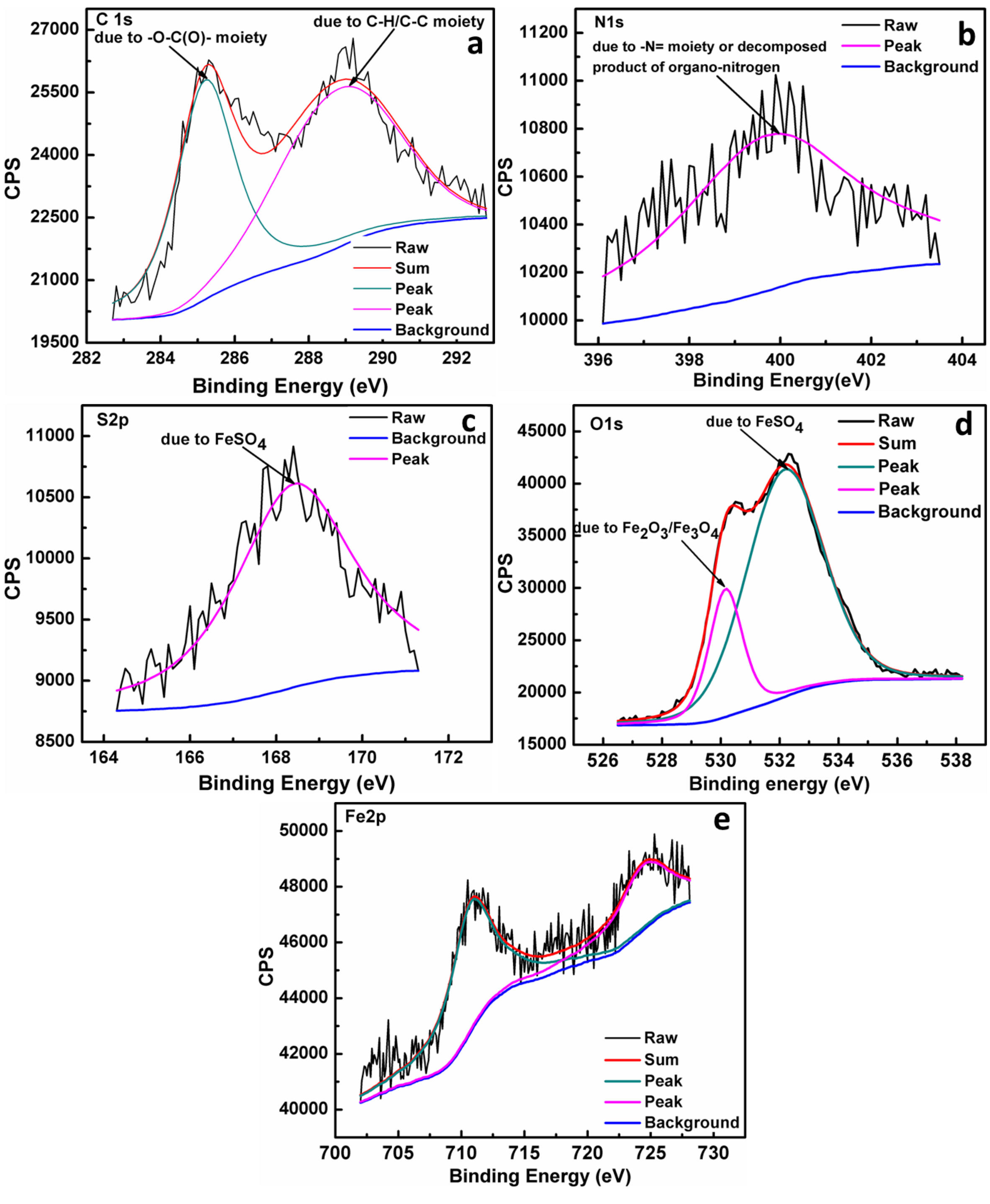



**Figure 3.14.** XPS spectra of tribochemical film formed on worn steel surface lubricated with cefixime additive (1% w/v) at 392 N applied load for 90 min. test duration in liquid paraffin. **(a).** C 1s **(b).**N 1s **(c).**S 2p **(d).** O 1s and **(e).** Fe 2p

### 3.3.4. Theoretical studies

Since the tested additives contain several other functional groups in addition to *β*-lactum ring, theoretical calculations have been performed to find out the effect of these groups towards their antiwear lubrication behavior. The data obtained for all quantum chemical parameters such as $E_{HOMO}$, $E_{LUMO}$, $\Delta E$, $\Delta E_1$ and $\Delta E_2$ are listed in Table 3.4. Frontier Molecular Orbital (FMO) theory is useful in predicting the adsorption behavior of the additive molecules which is responsible for interaction with metallic surface. Figure 3.15 shows that *β*-lactum antibiotics have different HOMO and LUMO distributions. HOMO density distributions are mainly localized around the aromatic ring of all *β*-lactum antibiotics except cephalexin, which might be due to the presence of hetero atom like N, O and S with π-electron in the additive molecules. High values of $E_{HOMO}$ are likely to indicate a tendency of the molecule to donate electron to appropriate accepter molecules with low energy and empty molecular orbital. On the other hand, $E_{LUMO}$ refers to the suitability of the molecule to accept electron, thus lower the value of $E_{LUMO}$, there is higher possibility that the electrons are accepted. As for the value of $\Delta E$ is concerned, it describes the minimum energy required to excite an electron from the HOMO. Therefore, lower the value of $\Delta E$, higher will be the tendency of the additive to get adsorbed. Thus $\Delta E$ is important quantum chemical parameter to correlate the experimental results with the theoretical ones. The obtained results (Table 3.4) indicate that the cefixime has the highest $E_{HOMO}$, lowest $E_{LUMO}$ and also lowest value of $\Delta E$ as compared to cefadroxil and cephalexin. On the basis of density functional theory parameters the order of *β*-lactum antibiotics as antiwear additives is as follows:-

Cefixime > Cefadroxil > Cephalexin

**Table 3.4.** Quantum chemical parameters for $\beta$-lactum antiwear additives calculated with B3LYP/6-31G++(dp) basis set

| **Additive** | **$E_{HOMO}$ (Hartree-fock)** | **$E_{LUMO}$ (Hartree-fock)** | **$\Delta E$ (Hartree-fock)** | **$\Delta E_1$ (Hartree-fock)** | **$\Delta E_2$ (Hartree-fock)** | **Wear rate ($10^{-4}$ x $mm^3/h$)** |
|---|---|---|---|---|---|---|
| $Fe_5$[Huang *et al*.(2003)] | -0.18651 | -0.06420 | 0.12231 | | | |
| Cefixime | -0.20657 | -0.10184 | 0.10473 | 0.08467 | 0.14237 | 16.60 |
| Cefadroxil | -0.23250 | -0.06807 | 0.16443 | 0.11844 | 0.16830 | 19.09 |
| Cephalexin | -0.24599 | -0.06509 | 0.18090 | 0.13560 | 0.18179 | 29.09 |

$\Delta E_1$= $E_{LUMO}$ of additive - $E_{HOMO}$ of iron

$\Delta E_2$= $E_{LUMO}$ of iron - $E_{HOMO}$ of additive

**Interaction with metallic surface**

A literature survey reveals that the adsorption of heterocyclic compounds on the metal surface can occur on the basis of donor-accepter interaction between the active centers of the heterocyclic compound and the vacant d-orbitals of metal atom [Jaiswal *et al*.(2014) and Heckerman *et al*.(1966)]. The investigated $\beta$-lactum lubricant additives are the polar molecules which get adsorbed onto the metal surface through their active sites. Therefore, for the investigation of antiwear behavior it is important to correlate molecular orbital energies of the additive molecules to those with the energy of metal [Rastogi *et al*.(2014) and Jaiswal *et al*.(2014)]. Huang *et al.*(2003) have calculated the energy of frontier molecular orbitals of iron by considering the iron as five-atom clusters. The interaction between additives and iron can be discussed on the basis of $\Delta E_1$ ($\Delta E_1$= $E_{LUMO}$

of additive - $E_{HOMO}$) and $\Delta E_2$ ($\Delta E_2$= $E_{LUMO}$ of iron – $E_{HOMO}$ of additive) as mentioned in Table 3.4. From these values it is evident that the additive molecules are electron donors while iron acts as an electron acceptor and this can be regarded as a nucleophilic reaction [Wang *et al.*(1982)]. The results show that the difference between $E_{HOMO}$ of cefixime and $E_{LUMO}$ of iron is smallest among all the three $\beta$-lactum additives, suggesting that the maximum interaction will take place between cefixime and iron. To be a good antiwear additive it is not only to donate the electron from HOMO of the additive molecules to the LUMO of the vacant d-orbitals of the iron atom but also there must be a significant interaction between the HOMO of the iron and LUMO of the additive molecules (Reterodonation/Backbonding). Since the antiwear additives are the polar molecules, the extent of interaction between $HOMO_{Additives}$ to $LUMO_{Iron}$ may always be higher than the $HOMO_{Iron}$ to $LUMO_{Additives}$. A greater transfer of electron density from additive molecules to the vacant d-orbital of iron atom accumulates the electron density on the iron. Consequently, it develops more tendencies to donate back electron to the vacant orbital of the additives. This favors the extent of backdonation (Synergistic bonding). It is evident from Table 3.4 that the values of interaction parameters $\Delta E_1$ ($E_{LUMO}$ of iron - $E_{HOMO}$ of additive) are always lower than $\Delta E_2$ ($E_{LUMO}$ of additives - $E_{HOMO}$ of iron) for all the $\beta$-lactum additives. The order of antiwear efficiency of $\beta$-lactum additives emerged on the basis of values of $\Delta E$, $\Delta E_1$ and $\Delta E_2$, is found to be exactly the same as that of their antiwear lubrication behavior evaluated experimentally with four ball tester.

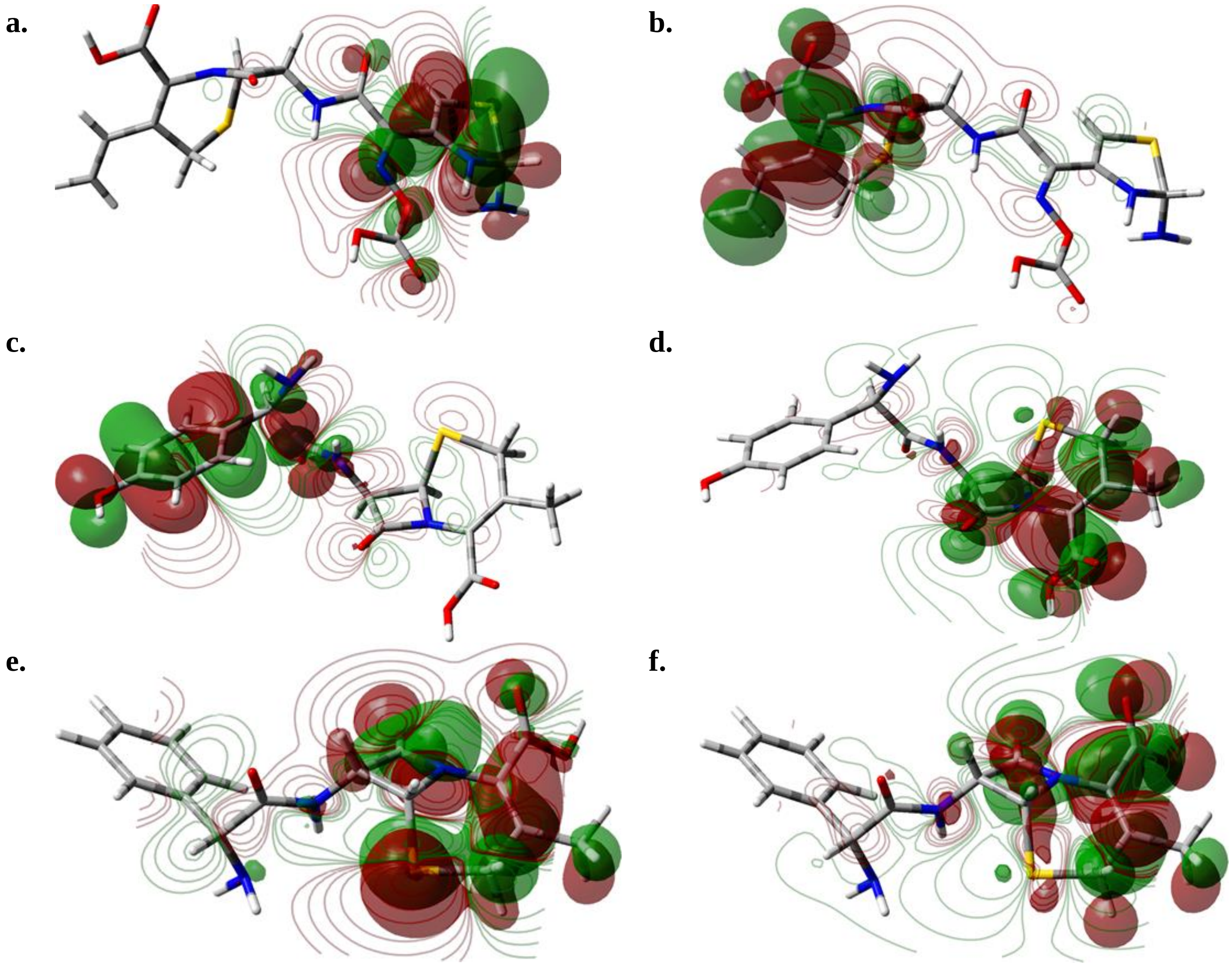



**Figure 3.15.** HOMO and LUMO density distributions of $\beta$-lactum additives respectively for (a,b). Cefixime, (c,d). Cefadroxil and (e,f). Cephalexin

## 3.4. Conclusions

- The addition of $\beta$-lactum antibiotics as an antiwear additive into neutral paraffin oil significantly improves its antiwear properties. The order of their efficiency towards antiwear behavior is as follows:

Cefixime > Cefadroxil > Cephalexin

- Among three $\beta$-lactum antibiotics, the overall, running-in and steady-state wear rates are found to be lowest in case of cefixime followed by cefadroxil, ZDDP and then cephalexin.
- The load carrying ability of the $\beta$-lactum antibiotics has been found to be much higher than paraffin oil alone and its admixture with ZDDP.
- Surface studies by SEM and AFM support the order of their antiwear properties.
- XPS analysis of the worn surface provides evidence in favor of formation of protective tribofilm containing N, S, O, Fe and C elements. It appears that there is strong adsorption of the additives and tribochemical reactions might have resulted in formation of a complex boundary lubrication film containing –O-C(O)-, C-C/C-H moieties, adsorbed organic-nitrogen and amide moiety, $FeSO_4$, $Fe_2O_3$ and/or $Fe_3O_4$ on the metallic surface.
- The density distributions of the frontier molecular orbitals (HOMO & LUMO) of the additive molecules obtained from quantum chemical calculations have been found to be in accordance with the experimental observations.
- The experimentally observed order of the antiwear properties of the additives can be fully explained in terms of theoretically calculated values of $E_{HOMO}$ and $E_{LUMO}$ values of the additives.