Ionic liquids (ILs), known for their applications as corrosion inhibitors [Espinosa et al. (2014)], nanoparticle stabilizers [Mu *et al*. (2005)] and used as solvents in green synthesis [Mu *et al.* (2005)] have attracted attention as lubricants/antiwear additives. The enhanced tribological behavior of ILs is due to their dipolar structure. In general, ILs reported in literature contain a large number of halogens (fluoride and bromide) and phosphorous atoms like 1-ethyl-3-hexylimidazolium tetrafluoroborate, tetraalkylphosphonium perchlorate, fluorinated hexaphenoxycyclotriphosphazene, alkylimidazoliumhexafluorophosphate, which limits their wide applications in the field of tribology [Gusain *et al*.(2014), Ge *et al*.(2015), Shah *et al*.(2009), Seddon *et al.*(2003), Espinosa *et al*.(2013) and Zhou *et al*.(2009)]. Thus, there is urgent need to develop some antiwear additives having least possible sulphated ash, phosphorous and sulfur contents (low SAPS) but possessing enhanced tribological properties.

This prompted us to synthesize a series of sulfur and phosphorous free quinoline based compounds having comparatively lower % of halogen and evaluate their tribological behavior in neutral paraffin oil using four-ball lubricant tester. These additives are also expected to enhance tribological properties of base oil as these would have a tendency to get adsorbed on the contact surfaces forming *in situ* a protective tribofilm which can bear the load under operating conditions. The obtained tribological results have been compared with those of ZDDP containing high SAPS. Besides this, quantum chemical calculations (QCC) have been performed for the synthesized additives to evaluate the interactions between additives and metal surface. A comparison of QCC results with the experimental observations supports the above interactions.

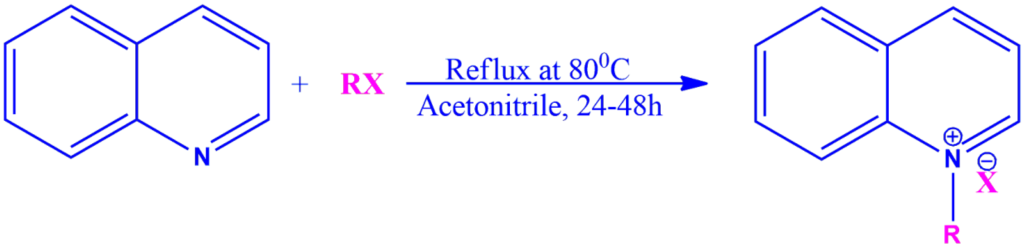
5.1. Materials & methods

5.1.1. Chemicals

For the synthesis of quinolinium compounds Methyl iodide (98.7%, Merck), propyl iodide (98%, Merck), N-Bromopropyl isoindolin-1,3-dione (99%, Hi-Media) and N-Bromoethyl isoindolin-1,3-dione (99%, Merck) were used as received.

5.1.2. Synthesis of Quinolinium compounds

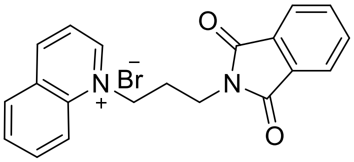
These compounds have been synthesized by the reported method [Lava *et al.*(2012)]. In a 100 ml round bottom flask, quinoline (5.0g, 0.039mol) and the corresponding halide (0.039mol) were taken in acetonitrile (50 ml). The reaction mixture was heated around 80-85^{o}C for 24-48 hours. The completion of reaction was checked by TLC (40% ethyl acetate and hexane). The solvent acetonitrile was evaporated by rotary evaporator. After evaporation, dark greenish or brown coloured solid compound appeared, it was recrystallized from methanol.



RX	Abbreviation
N-Bromopropyl isoindolin-1,3-dione	$[DIP\text{-}Q]^{+}Br^{-}$
N-Bromoethyl isoindolin-1,3-dione	$[DIE\text{-}Q]^{+}Br^{-}$
Iodopropane	$[P\text{-}Q]^{+}I^{-}$
Iodomethane	$[M\text{-}Q]^{+}I^{-}$

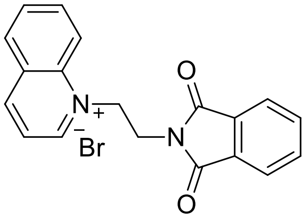
5.1.3. Analytical data of the synthesized Quinolinium compounds

1-(3-(1,3-dioxoisoindolin-2-yl)propyl)quinolin-1-ium bromide ([DIP-Q]$^+$ Br$^-$)



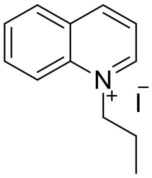
M.p. 245°C; **Yield:**12.4 g (80 %); **^{1}H-NMR (300 MHz, Si(CH$_3$)$_4$, CDCl$_3$):** δ3.73-3.78 (t, 2H,C$\underline{H}_2$), 3.94 (s, 2H, C$\underline{H}_2$), 5.39 (s,2H,C$\underline{H}_2$), 7.76-10.10 (m, 11H, ArC$\underline{H}$); **^{13}C NMR(75MHz, Si(CH$_3$)$_4$, CDCl$_3$):** δ27.2, 32.4, 40.6, 55.9, 113.7, 116.8, 121.7, 123.1, 134.1, 139.8, 143.2, 149.5, 165.7, 170.7, 186.1; **Elemental analysis for $C_{20}H_{17}BrN_2O_2$: Calcd:** C, 60.47; H, 4.31; N, 7.05; **Found:** C, 60.44; H, 4.28; N, 7.02%.

1-(2-(1,3-dioxoisoindolin-2-yl)ethyl)quinolin-1-ium bromide ([DIE-Q]$^+$ Br$^-$)



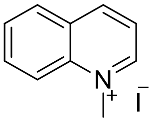
M.p. 252 °C; **Yield:**11.6 g (78 %); **^{1}H-NMR (300 MHz, Si(CH$_3$)$_4$, CDCl$_3$):** δ4.44-4.46 (t, 2H,C$\underline{H}_2$), 5.62 (t,2H,C$\underline{H}_2$), 7.75-10.00 (m, 11H, ArC$\underline{H}$); **^{13}C NMR(75MHz, Si(CH$_3$)$_4$, CDCl$_3$):** δ27.1, 32.2, 55.7, 113.8, 117.9, 122.0, 123.3, 134.4, 139.3, 143.6, 149.9, 165.9, 171.2, 186.2; **Elemental analysis for $C_{19}H_{15}BrN_2O_2$: Calcd:**C, 59.55; H, 3.95; N, 7.31; **Found:**C, 59.51; H, 3.90; N, 7.27%.

1-propylquinolin-1-ium iodide ($[P\text{-}Q]^+Br^-$)



M.p. 200°C; **Yield:** 10.4 g (90 %); **^{1}H NMR (300 MHz, $Si(CH_3)_4$, $CDCl_3$):** δ1.11-1.16 (t, 3H, C$\underline{H}_3$), 2.16-2.24 (q, 2H, C$\underline{H}_2$), 5.31-5.36 (t, 2H, C$\underline{H}_2$), 7.97-9.26 (m, 6H, ArC$\underline{H}$), 10.27-10.28 (s, 1H, Ar-C$\underline{H}$); **^{13}C NMR(75MHz, $Si(CH_3)_4$, $CDCl_3$):** δ10.9, 23.6, 59.5, 118.6, 122.3, 129.9, 130.3, 131.1, 136.2, 137.7, 147.4, 149.6; **Elemental analysis for $C_{12}H_{14}IN$: Calcd:** C, 48.18; H, 4.72; N, 4.68; **Found:** C, 48.16; H, 4.68; N, 4.65%.

1-methylquinolin-1-ium iodide ($[M\text{-}Q]^+I^-$)



M.p. 142°C; **Yield:** 8.9 g (85 %); **^{1}H-NMR (300 MHz, $Si(CH_3)_4$, $CDCl_3$):** δ4.94 (s,3H,C$\underline{H}_3$), 7.98-9.07 (m, 6H, Ar-CH), 10.32-10.33 (s, 1H, Ar-C$\underline{H}$); **^{13}C NMR(75MHz, $Si(CH_3)_4$, $CDCl_3$):** δ45.3, 118.6, 121.7, 126.3, 127.3, 130.4, 136.0, 138.0, 146.7, 149.8; **Elemental analysis for $C_{10}H_{10}IN$: Calcd:** C, 44.30; H, 3.72; N, 5.17; **Found:** C, 44.28; H, 3.69; N, 5.11%.

5.2. Results and Discussion

5.2.1. Additive optimization

The antiwear properties of the synthesized N-substituted quinoline based compounds, N(N-propyl-1,3-dioxoisoindolene)quinolinium bromide ($[DIP\text{-}Q]^+Br^-$), Npropylquinolinium iodide ($[\text{M-Q}]^{+}\text{I}^{-}$), N(N-ethyl-1,3-dioxoisoindolene)quinolinium bromide ($[\text{DIE-Q}]^{+}\text{Br}^{-}$) and N-methyl quinolinium iodide ($[\text{P-Q}]^{+}\text{I}^{-}$) in base oil were tested on four-ball tribometer. The additive concentration has been optimized before performing all tribological studies because tribological properties depend on the additive concentration in base oil. In all tribological tests, MWD has been measured for admixtures with additive concentrations 0.0, 0.5, 1.0 and 1.5% (w/v) in base oil at 392N applied load for 60 min duration. The results of additive optimization have been shown in Figure 5.1. It can be clearly seen from the figure that the largest MWD is observed in case of paraffin oil. For the surface lubricated with additives, in general, the value of MWD is always lower at all the experimental concentrations of additives showing that the quinolinium salts behave as efficient antiwear additives. At 0.5 % w/v concentration of the additives, there is drastic decrease in MWD for all the additives. As the additive concentration increases from 0.5 to 1.0 % w/v, the value of wear scar reduces further in each case. Thereafter, with increase in concentration up to 1.5%, there is no further significant reduction in MWD. It was found that the smallest MWD values for all the additives are obtained at 1.0% w/v. Therefore, all the tribological tests have been performed at 1% w/v additive concentration.

The decrease in the observed MWD values may be directly correlated with antiwear properties of the additives. Thus $[\text{DIP-Q}]^{+}\text{Br}^{-}$ shows better antiwear efficiency. The wear reducing property of the additive depends on concentration as well as their physico-chemical adsorption on metal surface to form *in situ* protective tribochemical film.

5.2.2. Antiwear testing

The measured MWD values of the contacting surface lubricated with quinolinium salts (1% w/v), ZDDP and paraffin oil alone (ASTM D 4172) are represented in the Figure

5.2. The largest value of MWD (0.681mm) was observed in case of pure paraffin oil. In presence of additives MWD is significantly reduced in all the cases. However, wear-resistance behavior of all the quinolinium compounds has been found to be much better than that of commonly used ZDDP. This is due to the fact that studied compounds are ionic molecules with a number of hetero-atoms which increases their competitive adsorption and reaction tendencies to form tribofilm improving their tribological performance in base oil. The observed MWD values of quinolinium derivatives show reduction by 36, 37, 45 and 51% for $[\text{M-Q}]^+\text{I}^-$, $[\text{P-Q}]^+\text{I}^-$, $[\text{DIE-Q}]^+\text{Br}^-$, $[\text{DIP-Q}]^+\text{Br}^-$ respectively, compared to plain paraffin oil. The triboactivity of these additives may be correlated well with their structures. It is well documented in the literature that as the access of number of active elements like nitrogen, sulfur, halogen, or alkyl chain and aromatic rings in the additive molecule to the metal surface increases, their tribological characteristics are also enhanced [Zhang *et al*.(1999)]. Additives $[\text{DIP-Q}]^+\text{Br}^-$ and $[\text{DIE-Q}]^+\text{Br}^-$ show better antiwear behavior than $[\text{P-Q}]^+\text{I}^-$ and $[\text{M-Q}]^+\text{I}^-$ which may be ascribed to the presence of additional 1,3-dioxoisoindoline moiety increasing their capability to get adsorbed on the metal surface. A slightly better antiwear properties of $[\text{DIP-Q}]^+\text{Br}^-$ than $[\text{DIE-Q}]^+\text{Br}^-$ may be due to presence of little longer propyl chain in the former and ethyl in the latter. Since $[\text{M-Q}]^+\text{I}^-$ is methyl derivative of quinolinium iodide and $[\text{P-Q}]^+\text{I}^-$ is its propyl analogue, the observed difference in their antiwear behavior may be similarly understood. Thus the order of different additives towards antiwear behavior is as follows:

$$[\text{DIP-Q}]^+\text{Br}^- > [\text{DIE-Q}]^+\text{Br}^- > [\text{P-Q}]^+\text{I}^- > [\text{M-Q}]^+\text{I}^- > \text{ZDDP} > \text{Paraffin oil}$$

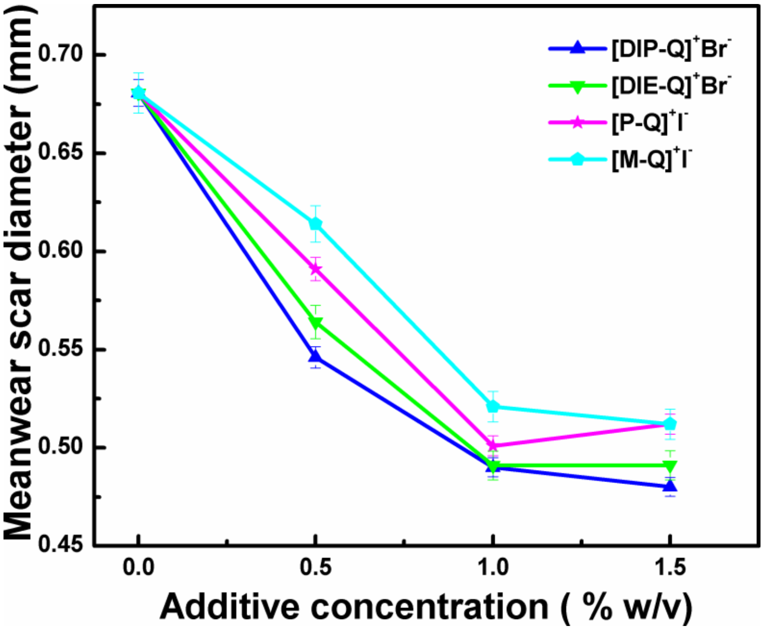


Figure 5.1. Variation of mean wear scar diameter in absence and presence of different concentrations of additives in paraffin oil at 392N applied load and 60 min duration

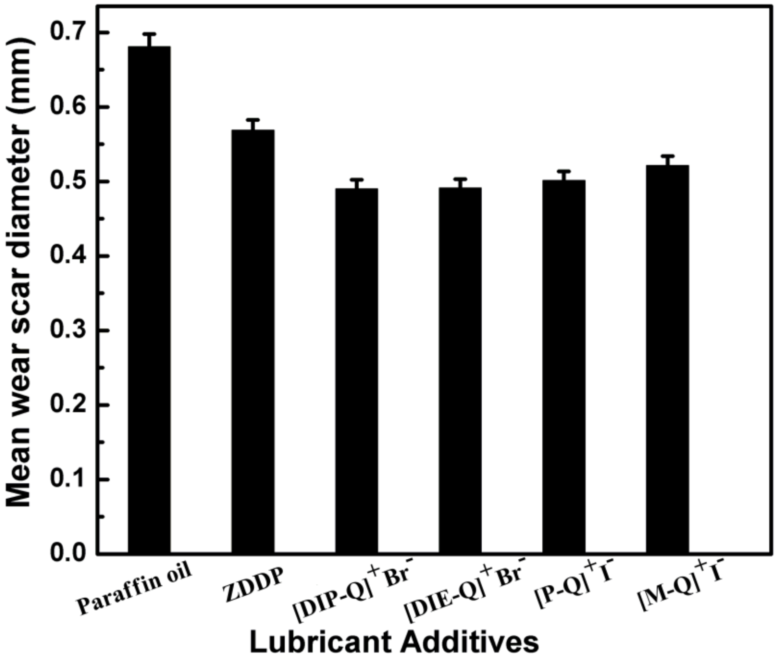


Figure 5.2. Variation of mean wear scar diameter in paraffin oil with and without different antiwear additives (1% w/v) at 392N applied load for 60 min test duration

In order to investigate the effect of time on friction and wear-resistance properties of synthesized quinolinium derivatives, a series of tribological tests have been conducted in paraffin oil at 392N applied load for different time durations with and without additives. Figure 5.3 shows the change in MWD values with different time exposure at 392N load (Table 5.1). It is apparent from Figure 5.3 that the value of MWD is much larger in the absence of additives for entire test durations. In general, the MWD values are reduced tremendously in presence of admixtures as compared to base oil. The activity of different quinolinium derivatives is well differentiated even at 15 min of run. Initially, for the 15 min of test duration, the value of MWD has been found to be larger in case of $[\text{M-Q}]^+\text{I}^-$ and $[\text{P-Q}]^+\text{I}^-$ with respect to ZDDP which in turn, is larger than those in case of $[\text{DIP-Q}]^+\text{Br}^-$ and $[\text{DIE-Q}]^+\text{Br}^-$. As the time increases from 15 to 30 min, there is sudden increase in MWD for base oil and its admixture with ZDDP while a small increment in MWD is observed in case of quinolinium derivatives. In between 30-75 min test duration, the extent of increment in the MWD values has significantly reduced in presence of quinolinium additives compared to ZDDP. For the last 15 min of test duration there is sudden increase in the MWD in case of ZDDP and base oil whereas a very small increase in MWD is observed for surface supplemented with quinolinium compounds.

The observed antiwear behavior of quinolinium compounds can be explained on the basis of formation of time dependent tribofilm [Cavdar *et al*.(1991)]. Initially, there is no tribofilm formed on the rubbing surfaces. With the passage of time, these quinolinium additives reacted with metal surface during tribo-contact and formed a protective tribofilm *in situ*.

Table 5.1. Tribological parameters for paraffin oil in the presence and absence of different 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.	[DIP-Q]$^+$ Br$^-$	0.366	01.248	0.402	02.361	0.423	03.186	0.435	03.722	0.435	03.722	0.457	04.838
4.	[DIE-Q]$^+$ Br$^-$	0.402	02.361	0.424	03.220	0.441	04.009	0.453	04.622	0.475	05.890	0.511	08.411
5.	[P-Q]$^+$ I$^-$	0.445	04.207	0.477	06.015	0.479	06.142	0.502	07.702	0.543	11.177	0.579	14.961
6.	[E-Q]$^+$ I$^-$	0.469	05.525	0.499	07.505	0.502	07.725	0.523	09.387	0.569	13.833	0.596	17.023

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

Figure 5.4 shows the changes in friction coefficient as a function of sliding time for the surface lubricated with admixtures of quinolinium salts and ZDDP (1% w/v) in paraffin oil. The friction coefficient values were found to be very high in case of blank paraffin. In contrast, the relatively much lower friction coefficient values were obtained for the surface supplemented with admixtures of quinolinium derivatives and ZDDP in paraffin oil. In every case, the values of coefficient of friction initially increase and after sometime get stabilized and/or decrease up to 60 min time duration. Subsequently, the COF abruptly increases till 90 min testing time.

For determining wear rate, mean wear volume was calculated using equation 2.3. To determine wear rate, the graph has been plotted between mean wear volumes versus time (h) and mentioned in Figure 5.5. The calculated values of running-in and steady-state wear rates have been tabulated in Table 5.2. The following order of wear rates was obtained for the tested additives:-

$$[\mathrm{DIP\text{-}Q}]^+\mathrm{Br}^- < [\mathrm{DIE\text{-}Q}]^+\mathrm{Br}^- < [\mathrm{P\text{-}Q}]^+\mathrm{I}^- < [\mathrm{M\text{-}Q}]^+\mathrm{I}^-$$

The observed order of wear rates confirm that $[\mathrm{DIP\text{-}Q}]^+\mathrm{Br}^-$ strongly adhered on the interacting surface forming tribochemical film, thereby causing maximum reduction in wear. Thus $[\mathrm{DIP\text{-}Q}]^+\mathrm{Br}^-$ proves to be the best antiwear additive as stated above.

Initially, in presence or absence of any additive there is material loss due to running-in stage where surfaces interact with each other adjusting corresponding asperities and valleys, therefore running-in wear rate is always high. In contrast, steady-state wear rate is expected to be lower. It can be stated that an antiwear additive is considered to be the best whose steady-state wear rate is found to be the lowest and it is achieved at the earliest. The observed values of both wear rates in presence of quinolinium derivatives were found to be lesser than those of ZDDP and base oil, Table 5.2. The behavior of running-in and steady-state wear rates is given in Figure 5.6 and Figure 5.7. In the present investigation, $[DIP\text{-}Q]^+Br^-$ shows minimum steady-state wear rate and thus, behaves as the best additive.

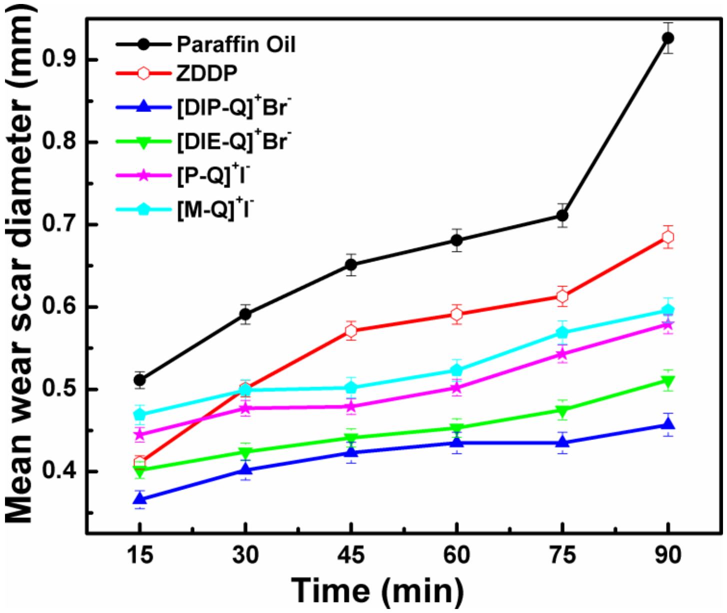


Figure 5.3. Variation of mean wear scar diameter with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP) and quinolinium derivatives at 392N applied load

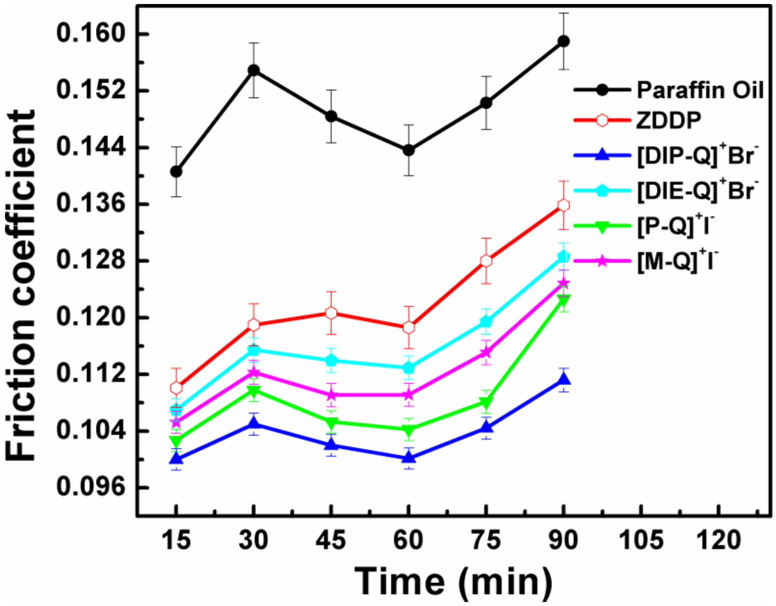


Figure 5.4. Variation of friction coefficient with time in paraffin oil containing (1%w/v) zinc dibutyldithiophosphate (ZDDP) and quinolinium derivatives at 392N applied load

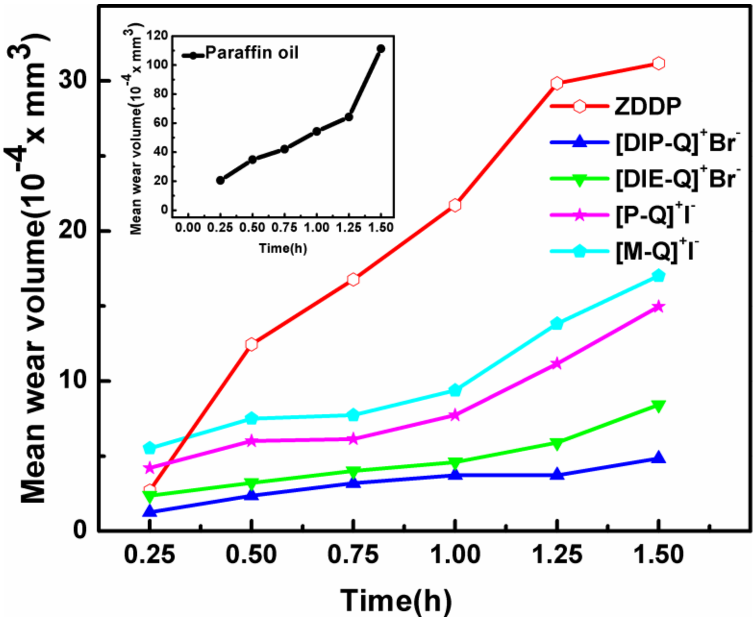


Figure 5.5. Variation of mean wear volume with time (h) in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP) and quinolinium derivatives at 392N applied load

Table 5.2. Wear rates of paraffin oil in absence and presence of quinolinium derivatives as 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
1.	[DIP-Q]$^+$Br$^-$	04.72	02.72
2.	[DIE-Q]$^+$Br$^-$	06.44	02.76
3.	[P-Q]$^+$I$^-$	12.03	03.42
4.	[M-Q]$^+$I$^-$	15.01	03.75
5.	ZDDP	24.92	18.52
6.	Paraffin oil	69.99	38.70

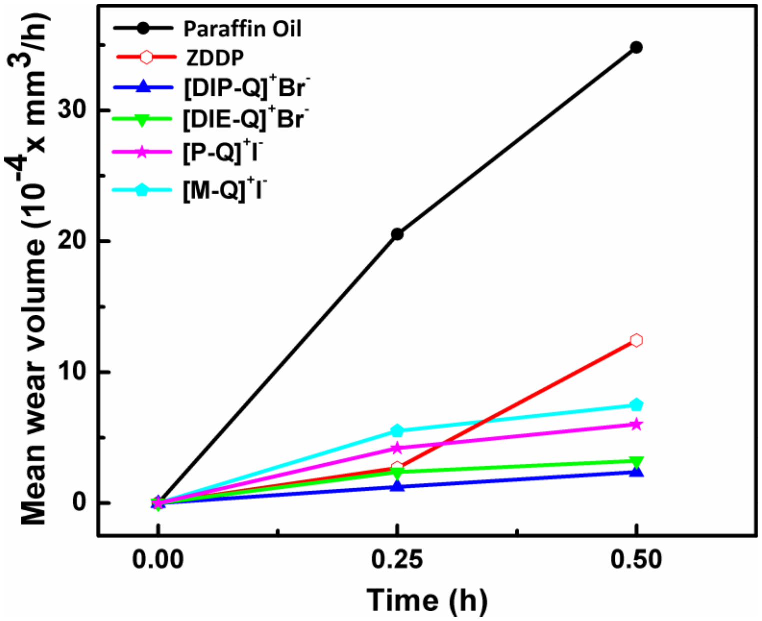


Figure 5.6. Determination of running-in wear rate by varying mean wear volume with time (h) in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate and quinolinium derivatives at 392N applied load

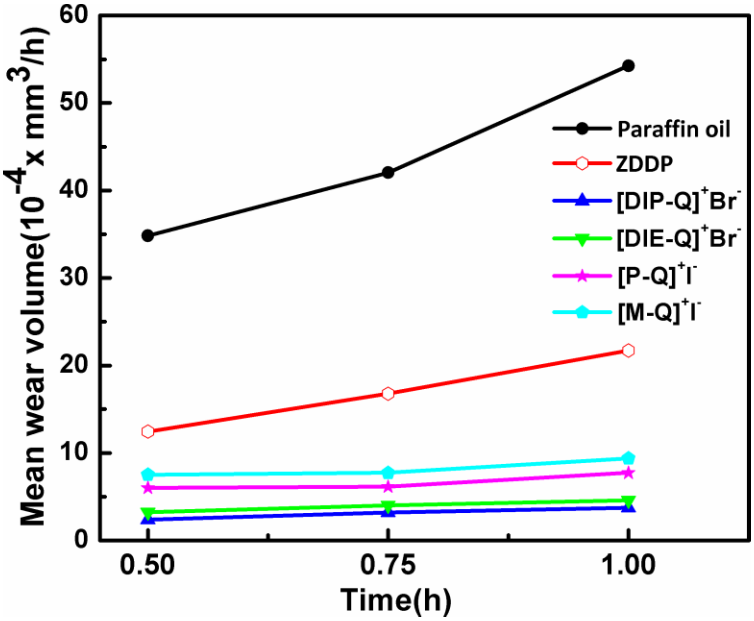


Figure 5.7. Determination of steady-state wear rate by varying mean wear volume with time (h) in paraffin oil containing (1% w/v) with and without additives at 392N applied load

5.2.3. Effect of load

The performance of these additives as a function of load has been evaluated at different loads 294, 392, 490, 588 and 686N for 30 min of test duration in paraffin oil. The variation of MWD vs. applied load at 30 min test duration is shown in Figure 5.8. The values of MWD are found to be maximum in plane paraffin oil at each load while these are minimum in case of quinolinium salts. It is noticeable from the figure that the MWD increases invariably in all cases up to 490N applied load but the slopes of curves are widely different. The slope is the highest for base oil, the lowest for quinolinium salts and for ZDDP it lies in between. This behavior can be explained on the basis of better adsorption of the additives on the metallic surfaces as compared to ZDDP/base oil. Thus, thin film of the additives adsorbed on the metal surface protects it from wear. On further increasing the load after 490N, the tribofilm is unable to bear the load when it is plain paraffin. When the surface is supplemented with ZDDP, the MWD increases but the tribofilm formed is comparatively stronger and bears the load up to 588N. In presence of admixtures of quinolinium compounds in paraffin oil, there is slight increment in the MWD value; however, these compounds bear the load up to 686N indicating that the tribofilm formed is the strongest and the most adherent.

5.2.4. Surface Characterization

5.2.4.1. Surface morphology

The topography of the worn surface has been examined by scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM). Herein, for comparison purposes the SEM and AFM images of better additives from each category of halides i.e. $[\text{DIP-Q}]^+\text{Br}^-$ (from bromides) and $[\text{M-Q}]^+\text{I}^-$ (from iodides) have been selected. The SEM images of the wear track supplemented with or without additives (1% w/v) at 392N load for 90 min test run are exhibited in Figure 5.9. The SEM-micrographs for base oil in presence and absence of different additives are shown in Figure 5.9a and Figure 5.9(b-d). Figure 5.9 illustrates that the surface has undergone severe destruction in paraffin due to absence of any protective tribochemical film while it is much smoother in presence of additives. However, the extent of surface smoothening in case of surface supplemented with quinolinium derivatives has been found to be much better than ZDDP due to the formation of adherent *in situ* tribochemical film which eventually filled the irregularities of surfaces. Thus, the investigated additives prove to be potential antiwear additives. It can be vividly seen in the micrographs that the surface roughness has tremendously reduced in case of $[DIP\text{-}Q]^+Br^-$ (Figure.9c) where the furrows formed are quite small. On the other hand, the furrows of comparatively larger and deeper nature are observed in case of $[P\text{-}Q]^+I^-$ (Figure 5.9d).

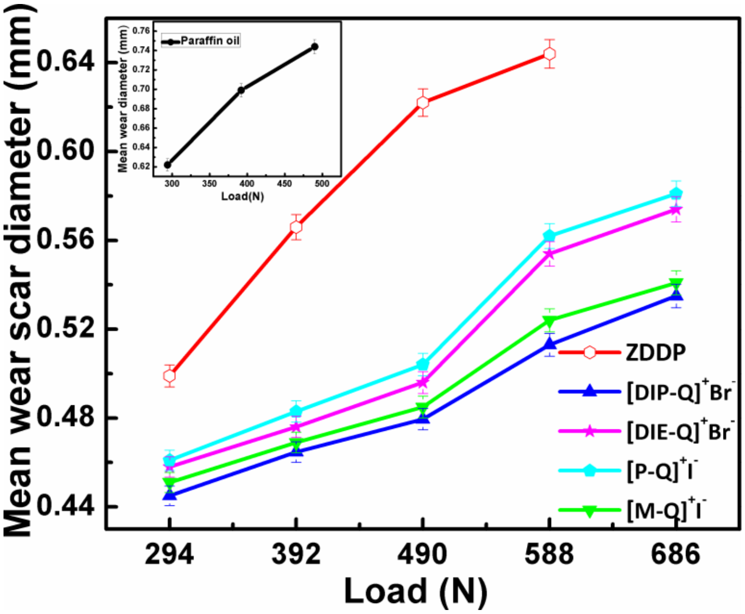


Figure 5.8. Variation of mean wear scar diameter with applied load in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP) and quinolinium derivatives for 30 min test duration

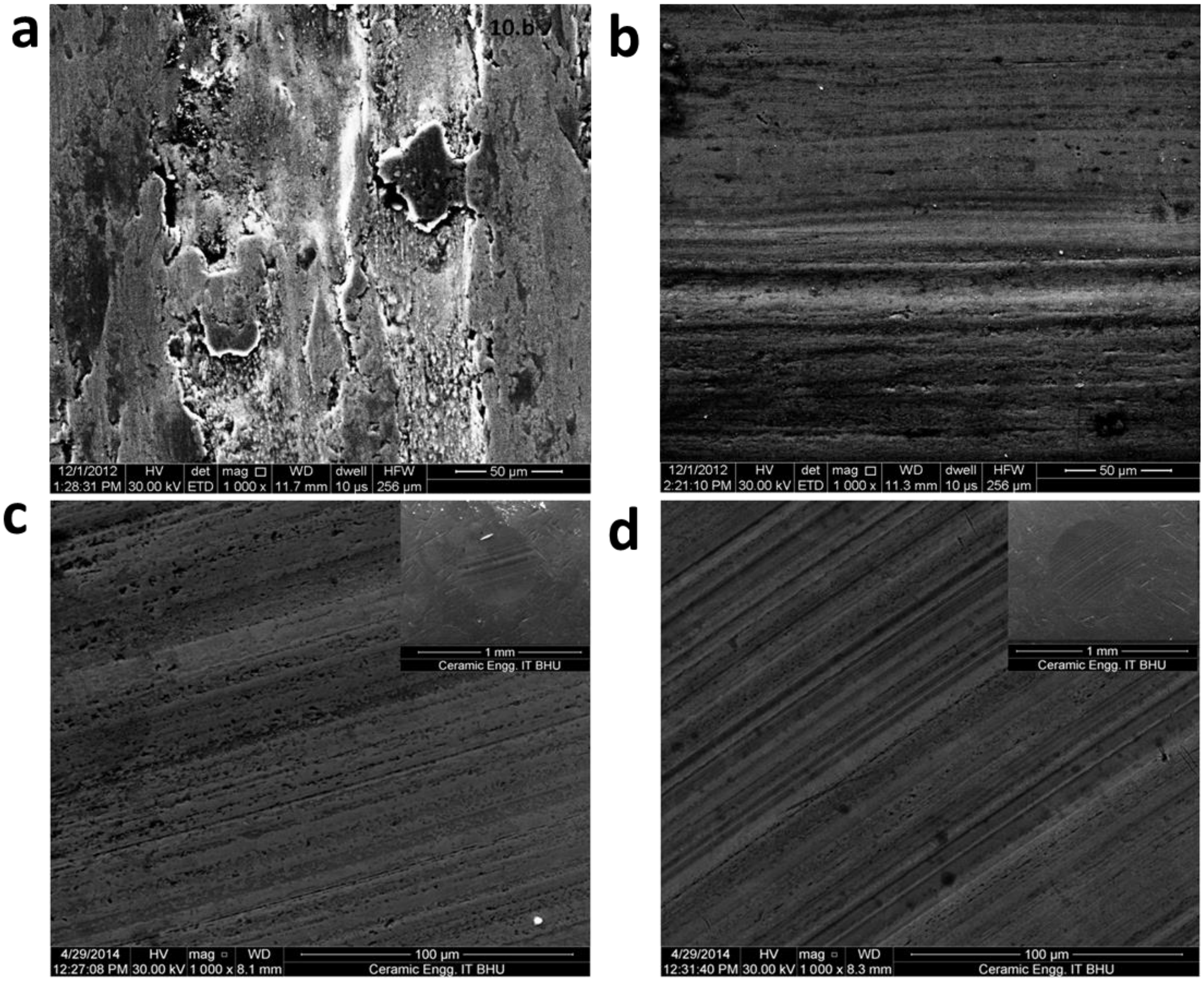


Figure 5.9. SEM micrographs at different magnifications of the worn steel surface lubricated with different additives (1% w/v) in paraffin oil for 90 min. test duration at 392N applied load: (a) Paraffin oil, (b) ZDDP, (c) $[\text{DIP-Q}]^+\text{Br}^-$ and (d) $[\text{P-Q}]^+\text{I}^-$

For understanding the behavior of these additives, the SEM studies were performed at higher load 588N and 30 min time period. From the micrographs displayed in Figure 5.10 it can be inferred that the trend of additives towards surface smoothening is similar to that as obtained at 392N load for 90 min time duration. The antiwear property of additives can be interpreted similarly. Thus, the suitability of these quinolinium derivatives at higher load is fully supported by these SEM-images.

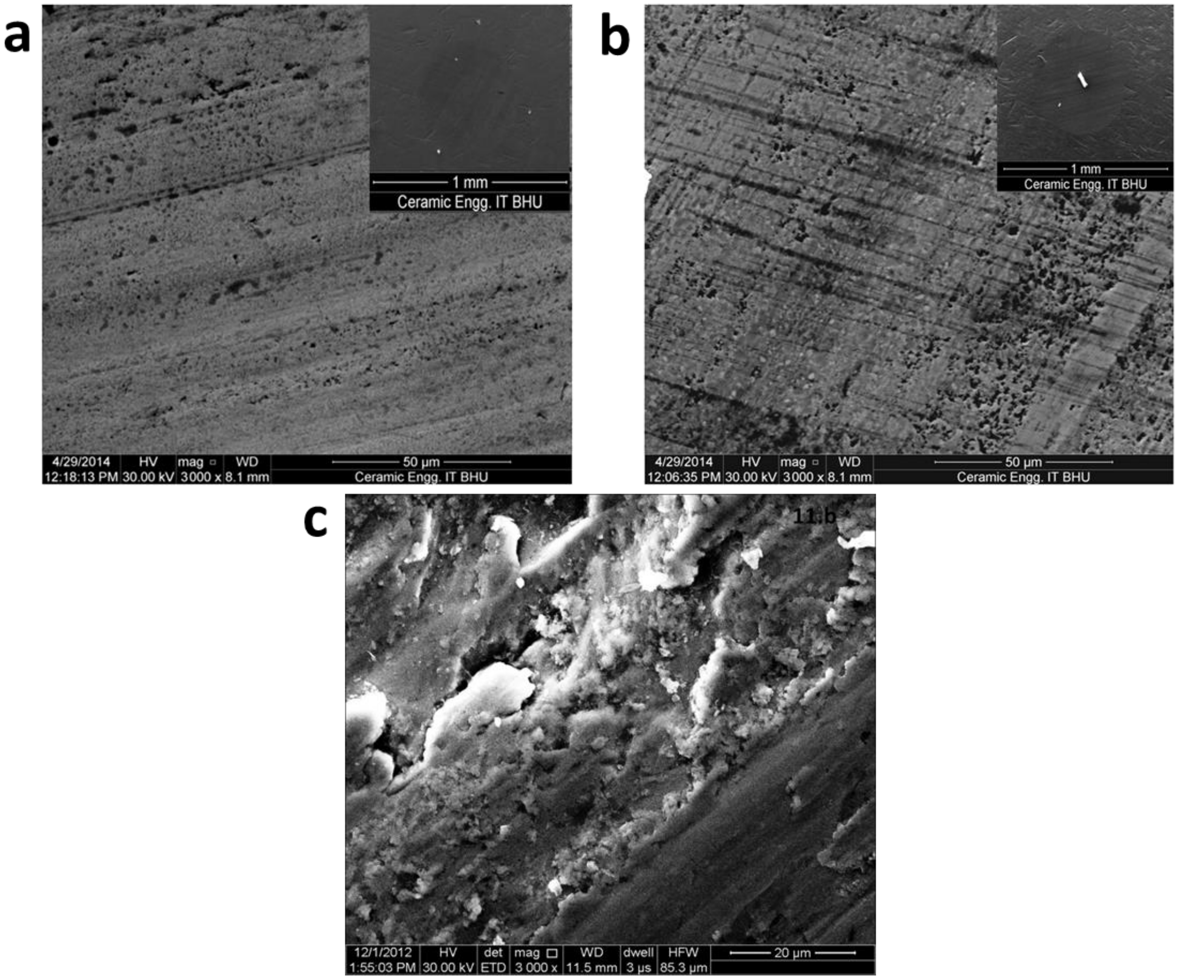


Figure 5.10. SEM micrographs of the worn steel surface lubricated with (a) [DIP-Q]$^+$Br$^-$ (b) [P-Q]$^+$I$^-$ and (c) ZDDP (1% w/v) in paraffin oil for 30 min test duration at 588N applied load

Surface undulations of the wear scar lubricated with paraffin oil and blends of additives after the tribological tests were studied by contact mode AFM at 392N load for 90 min test duration, the images thereof are exhibited in Figure 5.11 (a-d) and corresponding relevant data are mentioned in Figure 5.12. In case of paraffin oil, both the area as well as line roughness are significantly high whereas these have appreciably reduced in presence of ZDDP and new additives. A large plateau is observed for the surface supplemented with base lube (Figure 5.11a) showing large differences in the average peak-valley height (2.63μm) whereas very small surface undulations are observed in case of ZDDP (635.02nm), Figure 5.11b. Moreover, in presence of additive $[DIP\text{-}Q]^{+}Br^{-}$, the average value of peak-valley height (346.51nm) was found to be lower than $[P\text{-}Q]^{+}I^{-}$ (402nm). The area roughness has been found to be largest (Sq=409 nm) for the base oil followed by ZDDP (Sq=75 nm) and then $P\text{-}Q]^{+}I^{-}$ (Sq= 51nm), $[DIP\text{-}Q]^{+}Br^{-}$ (Sq= 24nm). Thus, the AFM-images also support the observed results of tribological tests. The micrographs obtained at higher loads 588N show that surface roughness has increased in every case (Figure 5.13).

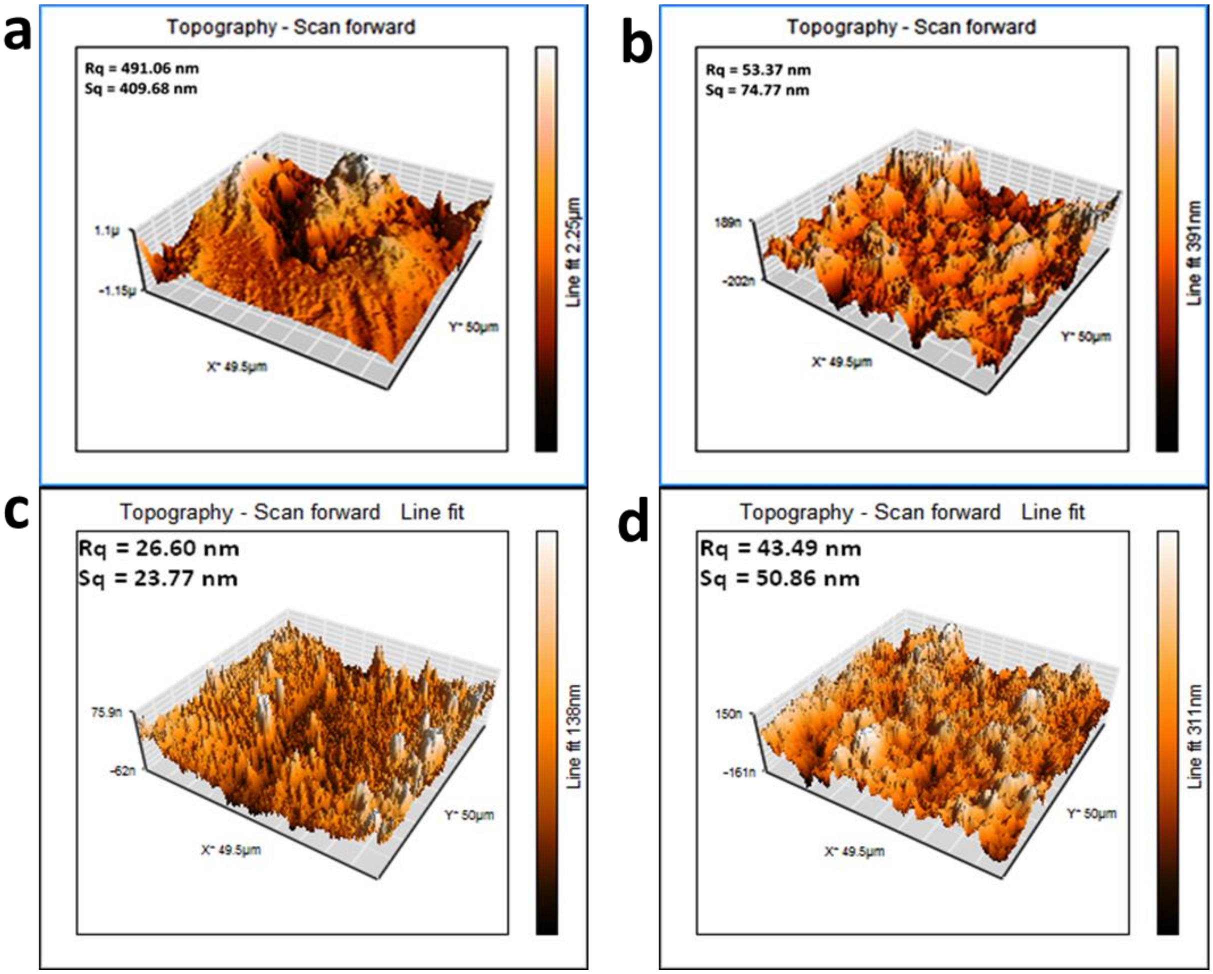


Figure 5.11. 3*D*-AFM images of the worn steel surface lubricated with different additives (1% w/v) in paraffin oil for 90 min. test duration at 392N applied load: (a) Paraffin oil (b) ZDDP (c) $[DIP\text{-}Q]^{+}Br^{-}$ and (d) $[P\text{-}Q]^{+}I^{-}$

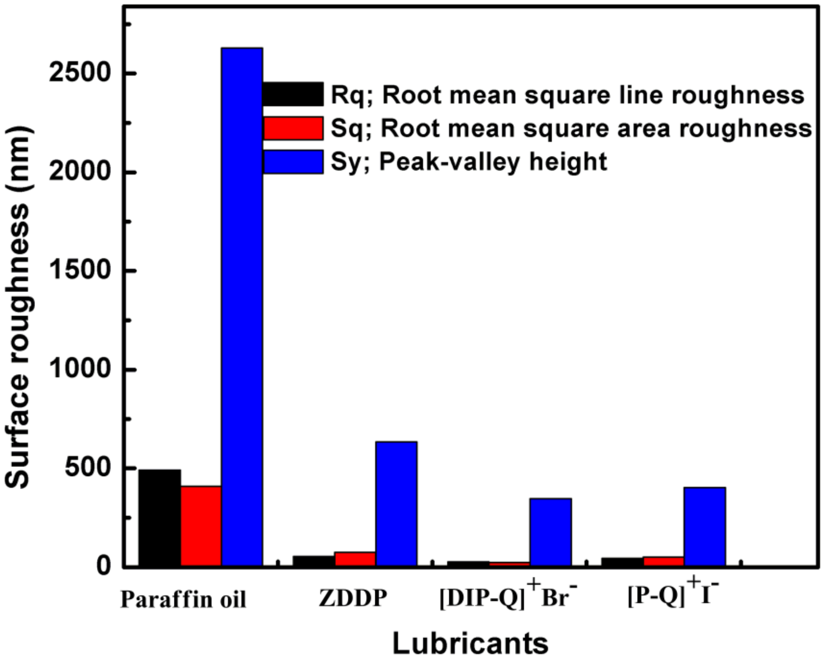


Figure 5.12. Surface Roughness parameters obtained from digital processing software of Nanosurf-basic Scan 2 for different additives at 392N load for 90 min. test duration

5.2.4.2. Tribochemistry

The EDX analysis has been carried out to find out the elemental compositions of the wear scar in presence and absence of ZDDP, $[DIP\text{-}Q]^+Br^-$ and $[P\text{-}Q]^+I^-$in base oil at 392N load for 90 min test time and the resulting images are presented in Figure 5.14(a-d). It is apparent from the figure that worn surface supplemented with base oil alone shows presence of only oxygen, carbon and iron. The presence of oxygen may be due to the oxide formation. The tribofilm is composed of hetero-atoms such as zinc, phosphorous and sulphur in case of ZDDP. The elemental composition of wear scar surfaces lubricated with $[DIP\text{-}Q]^+Br^-$ and $[P\text{-}Q]^+I^-$ shows the presence of bromide/iodide, nitrogen, iron and oxygen on the wear track confirming the formation of *in situ* protective tribochemical film. Besides this, the superior tribological behavior of $[DIP\text{-}Q]^+Br^-$ over $[P\text{-}Q]^+I^-$ can be easily understood from the elemental data provided with the EDX-images. As apparent from the Figure (5.14 c and d), a greater atomic percentage of bromide, nitrogen and oxygen in case of [DIP-Q]$^+$Br$^-$ than that for [P-Q]$^+$I$^-$ indicates that a stronger tribofilm was formed on the contact surface lubricated with [DIP-Q]$^+$Br$^-$. This has been the culmination of its interaction with metal surface forming protective film which reduces friction and wear.

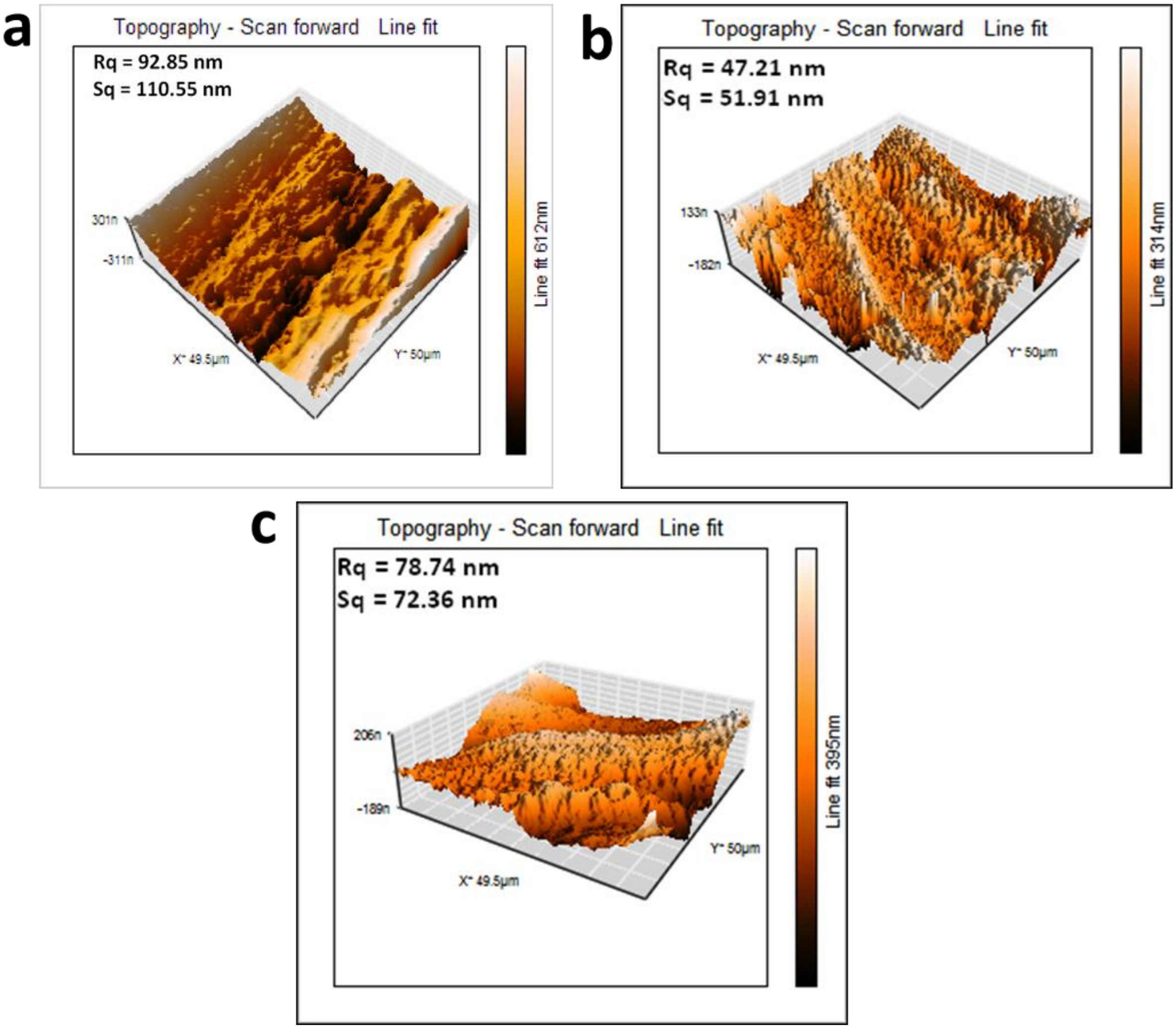
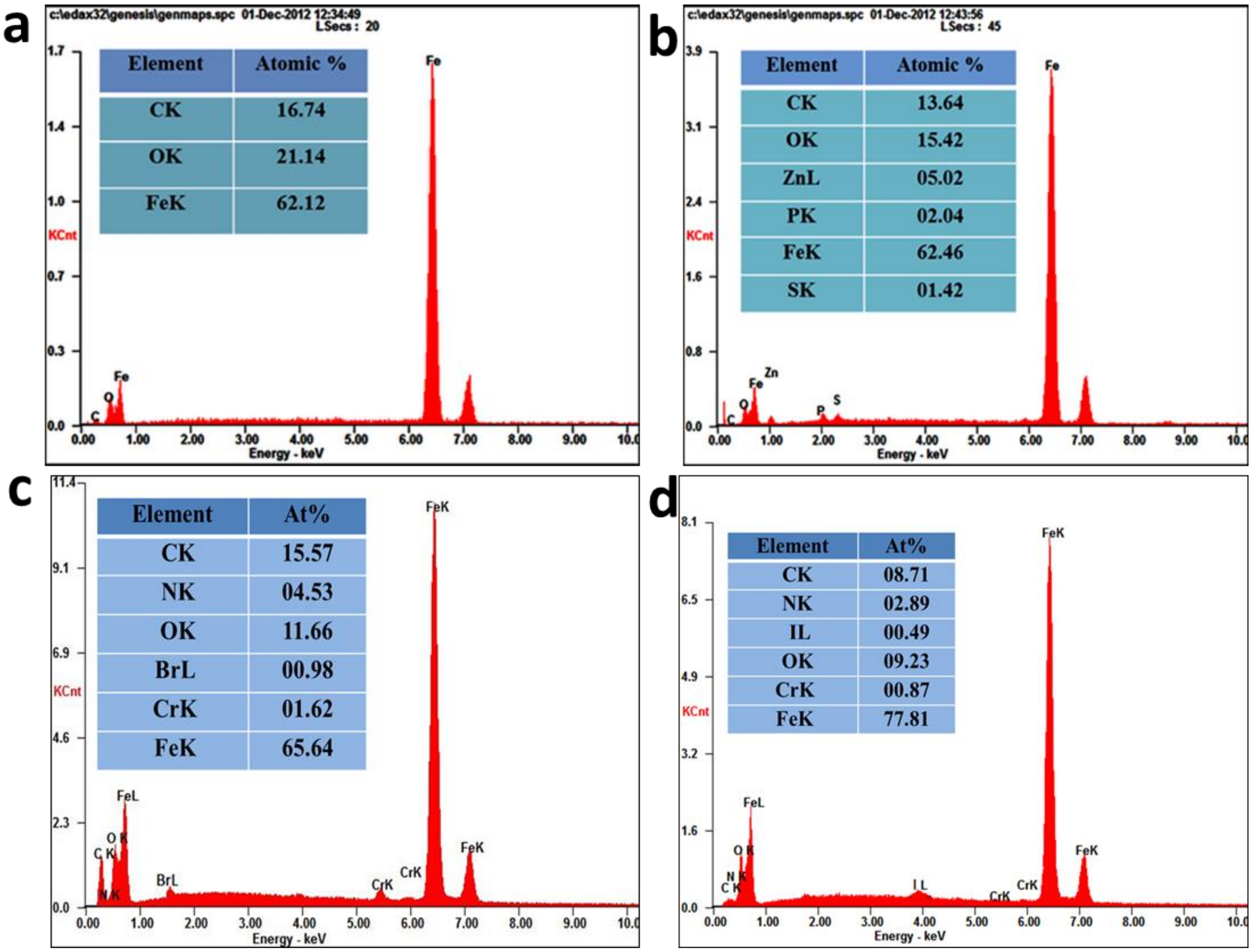


Figure 5.13. 3*D*-AFM images of the worn steel surface lubricated with different additives (1% w/v) in paraffin oil for 30 min. test duration at 588N applied load: (a) ZDDP (b) [DIP-Q]$^+$Br$^-$ and (c) [P-Q]$^+$I$^-$



(a)

Element	Atomic %
CK	16.74
OK	21.14
FeK	62.12

(b)

Element	Atomic %
CK	13.64
OK	15.42
ZnL	05.02
PK	02.04
FeK	62.46
SK	01.42

(c)

Element	At%
CK	15.57
NK	04.53
OK	11.66
BrL	00.98
CrK	01.62
FeK	65.64

(d)

Element	At%
CK	08.71
NK	02.89
IL	00.49
OK	09.23
CrK	00.87
FeK	77.81

Figure 5.14. EDX analysis data of the worn steel surface lubricated with paraffin oil in presence and absence of different additives (1% w/v) for 90 min. test duration at 392N applied load: (a) Paraffin oil, (b) ZDDP, (c) $[\text{DIP-Q}]^+\text{Br}^-$ and (d) $[\text{P-Q}]^+\text{I}^-$

To study the tribochemistry of additive at metal-metal interface, XPS analysis of the wear scar in presence of $[\text{DIP-Q}]^+\text{Br}^-$ at 392N load for 60 min test duration has been performed. The XPS analysis confirms that the wear preventive tribofilm was composed of C, N, O, Br and Fe elements. Figure 5.15 shows the XPS spectra of C1s, N1s, Br3d, O1s and Fe2p of the tribofilm. The spectrum of C1s on the worn surface exhibits peaks at 287.45 eV corresponding to carbonyl bonds [Hyong *et al*.(2012a)]. The binding energy of N1s is about 400.28 eV which shows that the nitrogen is in the form of decomposition products (imine bonds) of the organo-nitrogen moiety [Hyong *et al*.(2012b)]. The spectrum of $Br3d_{3/2}$ on the worn surface indicates the existence of a peak at around 70.3eV. On combining the $Br3d_{3/2}$ peak with the binding energy 710.1eV of the $Fe2p_{3/2,}$ the formation of *in situ* $FeBr_3$ film is confirmed during the tribochemical reaction [Grosvenor *et al*.(2004)]. Furthermore, combining the binding energies of O1s at 530.2 eV with Fe2p at 723.5 eV, it can be inferred that iron has oxidized to Fe_3O_4 during the rubbing process [Li *et al*.(2010)]. Thus, $FeBr_3$, Fe_3O_4 and decomposition products of nitrogen, as the major constituents of tribofilm, are mainly responsible for improving the antiwear behavior of the $[DIP\text{-}Q]^+Br^-$ additive in paraffin oil.

5.2.5. Theoretical studies

Quantum chemical calculations of the studied quinolinium derivatives have been performed to give some insight into the effect of change of various substituents around basic quinolinium skeleton on antiwear properties [Karelson *et al*.(1996), Huang *et al*.(2003) and Domingo *et al*.(2013)]. The obtained data such as E_{HOMO}, $E_{LUMO,}$ ΔE and ΔE_{Fe-A} are listed in Table 5.3. Tendency of the additives to get adsorbed on the metallic surfaces depends upon availability of electrons on the donor-atoms due to varying substituents, steric approach etc. According to Frontier Molecular Orbital theory (FMO), the energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}) and their energy difference (ΔE) for an additive play together important role in describing its tribological properties [Wang *et al*.(2007)]. Higher value of E_{HOMO} for an additive signifies its better electron donating tendencies while lower value of E_{LUMO} is responsible for its better acceptable behavior. A high energy gap (ΔE) corresponds to high stability of the additives thereby such compounds show least affinity towards interaction with metal surfaces. An additive with high value of E_{HOMO} but comparatively lower values of E_{LUMO} and ΔE is supposed to have maximum interaction with the metal surface and therefore expected to show significant tribological behavior.

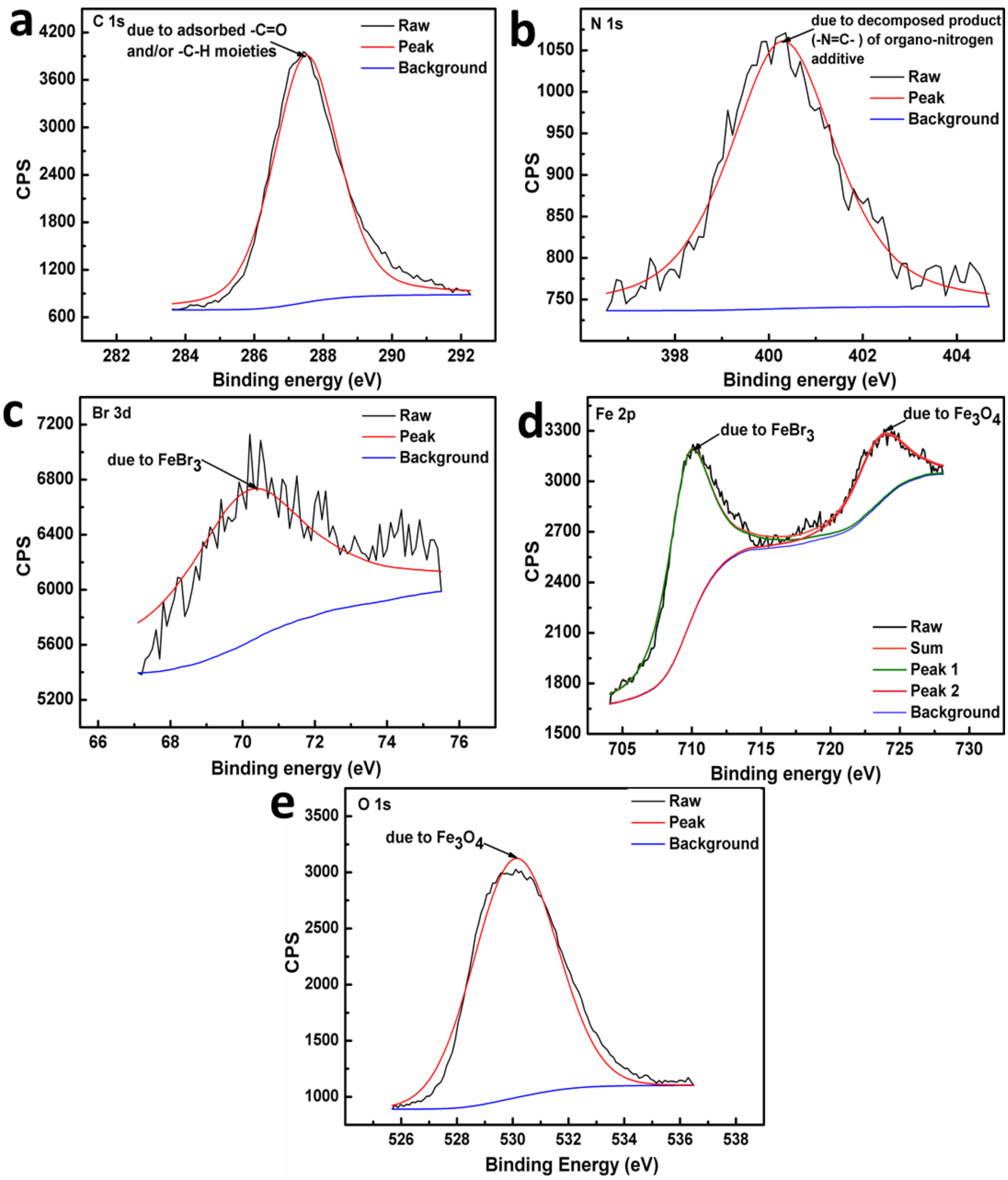


Figure 5.15. XPS spectra of tribochemical film formed on worn steel surface lubricated with the [DIP-Q]$^+$Br$^-$ additive (1%w/v) at 392N applied load for 90 min. test duration in liquid paraffin. (a) C1s (b) N1s (c) Br3d$_{3/2}$ (d) Fe2p and (e) O1s

Table 5.3. Quantum chemical parameters for quinolinium derivatives as antiwear additives calculated with B3LYP/DGTZVP basis set

Additives	**E_{HOMO} (Hartree)**	**E_{LUMO} (Hartree)**	**ΔE (Hartree)**	**ΔE_{Fe-A} (Hartree)**	**Running-in wear rate (10^{-4} x mm^3/h)**
Fe_5[Huang *et al*.(2003)]	-0.18651	-0.06420	0.12231		
$[DIP\text{-}Q]^+Br^-$	-0.19452	-0.10776	0.08676	0.13032	04.72
$[DIE\text{-}Q]^+Br^-$	-0.19606	-0.10486	0.0912	0.13186	06.44
$[P\text{-}Q]^+I^-$	-0.19658	-0.09613	0.10045	0.13238	12.03
$[M\text{-}Q]^+I^-$	-0.19981	-0.09759	0.10222	0.13560	15.01

$\Delta E = E_{LUMO}$ of additive - E_{HOMO} of additive
$\Delta E_{Fe\text{-}A} = E_{LUMO}$ of iron - E_{HOMO} of additive

From the Table 5.3, it can be clearly seen that in comparison to other additives, $[DIP\text{-}Q]^+Br^-$ shows the highest E_{HOMO}, lowest E_{LUMO} and ΔE. Thus, $[DIP\text{-}Q]^+Br^-$ is more prone to get adsorbed on to the metal surface to form protective tribochemical film which makes it excellent lubricant additive.

Thus antiwear behavior of quinolinium derivatives follows the order given below:-

$[DIP\text{-}Q]^+Br^- > [DIE\text{-}Q]^+Br^- > [P\text{-}Q]^+I^- > [M\text{-}Q]^+I^-$

The distributions of electron density on the frontier molecular orbitals of quinolinium derivatives are mentioned in Figure 5.16. These FMO-images show that the quinolinium derivatives have different electron density distributions around their HOMO and LUMO. In all cases, the HOMO density distributions are mainly localized around respective halide anion, quinolinium moiety hetero atom and its π-electrons. The contribution towards density distributions to LUMO in $[DIP\text{-}Q]^+Br^-$ and $[DIE\text{-}Q]^+Br^-$ is provided by 1,3-dioxo isoindoline moiety only, however, in case of $[P\text{-}Q]^+I^-$ and $[M\text{-}Q]^+I^-$ the entire molecule is involved.

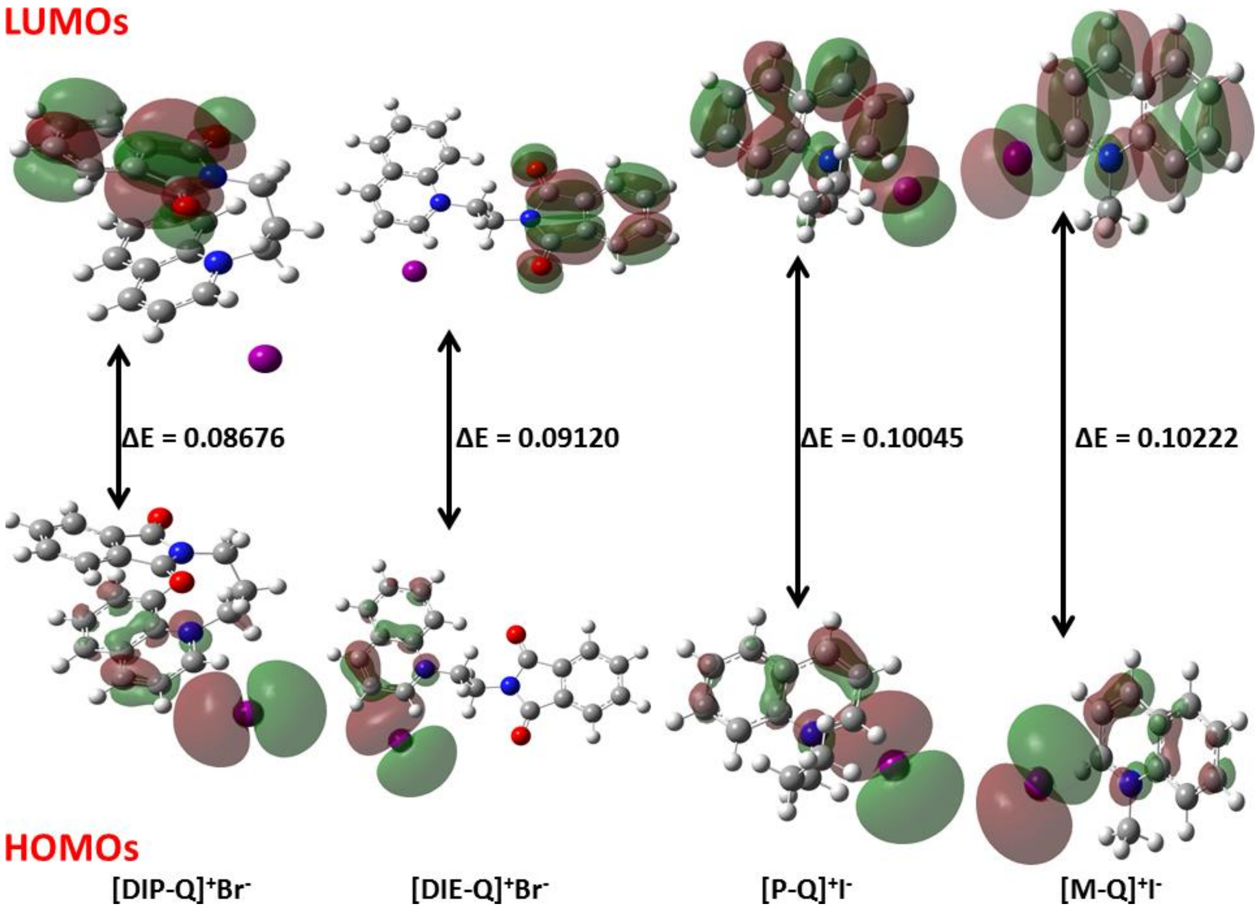


Figure 5.16. Frontiers molecular orbital images (HOMO and LUMO) of different quinolinium derivatives

5.2.5.1. Interaction with metallic surface

To investigate the lubrication mechanism, the interactions of additives with the metal surface have been explored and a comparison between frontier molecular orbitals of iron and additive molecules has also been made. In general, there is donation of electron density from the active centres of the additive molecules to the empty d-orbitals of metal atom [Jayadas *et al*.(2006) and Eddy *et al.(*2011)]. The difference in energy between E_{LUMO} of iron and E_{HOMO} of additive (ΔE_{Fe-A}), tabulated in Table 5.3, has been considered as a parameter of interaction between the two and found to be minimum in case of $[DIP\text{-}Q]^+Br^-$.

Thus, $[DIP\text{-}Q]^+Br^-$ undergoes maximum interaction and hence acts as the best antiwear additive.

5.3. Conclusions

The tribological properties of paraffin oil blends of quinolinium compounds which are devoid of Sulphated Ash, Phosphorous and Sulfur (SAPS free) have been evaluated in a four ball tribotester using ZDDP as a reference additive. The above tribological results suggest that both antifriction and antiwear properties for the optimal concentration of quinolinium compounds in paraffin base oil have dramatically improved than that of ZDDP. Besides this, these quinolinium compounds possess superior load bearing ability and wear reducing behavior on metal surfaces compared to ZDDP. Among the studied quinolinium compounds, the best antiwear performance has been achieved in case of surface lubricated with $[DIP\text{-}Q]^+Br^-$ followed by $[DIE\text{-}Q]^+Br^-$, $[P\text{-}Q]^+I^-$ and then $[M\text{-}Q]^+I^-$. Results of SEM and AFM studies are in conformity with the above order. The EDX-analysis of worn surface confirmed that the tribofilm is made up of bromide/iodide, nitrogen and oxygen. The XPS analysis of worn surfaces in presence of quinolinium additives shows that tribofilm is composed of $FeBr_3$, Fe_3O_4 and organic compounds containing carbonyl and imine bonds. The various quantum chemical interaction parameters for investigated quinolinium salts with metal surface are in agreement with the experimentally observed antiwear results. These new additives being SAPS-free, possess potentiality towards engines as well as exhaust after treatment devices since these are supposed not to interfere with the efficiency of catalytic convertors.