

# **CHAPTER-II**

## **Ionic liquid as a multifunctional lubricating oil additive**

### **2.1.1. Introduction**

Ionic liquids (more specifically, room temperature ionic liquids (RTIL)) have attracted great interest over the last several years. Ionic liquids (ILs) are broadly referred to as molten salts in liquid state. Generally ILs are a specific type of liquid salts with melting temperatures lower than 100<sup>0</sup>C (212<sup>0</sup>F). Unlike ordinary liquids such as water or alcohol, ILs are mostly composed of charged ions as opposed to electrically neutral molecules.

Ionic liquids have many good features<sup>1-5</sup> such as low volatility, non-flammability, low combustibility, high ionic conductivity, high thermo-oxidative stability, eco-friendly etc. Therefore, they should be ideal candidates for new lubricants, suitable for use in severe conditions where conventional oils and greases or solid lubricants fail.

ILs have been the subject of research and development for quite a long time. Ionic liquids (ILs) were first reported<sup>6</sup> as very promising high-performance lubricants in 2001 and have attracted considerable attention in the field of tribology since then because of their remarkable lubrication and anti-wear capabilities as compared with lubrication oils in general use.<sup>7</sup> In recent times, we have seen dramatically increased interest in this topic.

The choice of cation and anion in an ionic liquid (IL) as well as the design of ion side chains regulate the fundamental properties of ILs, which permits creating suitable lubricants and lubricant additives.<sup>8</sup> Limited results of very recent studies have shown the potential for using ionic liquids as a new class of lubricants.<sup>5-7</sup> Friction and wear reductions have been reported on metallic and ceramic surfaces lubricated by selected ionic liquids compared to conventional hydrocarbon lubricants. It was also suggested that adding a few percent of ionic liquids could improve the lubricating performance of base oils or water.

Over the last 15 years, research interest in ILs has expanded into lubrication due to their potential performance as neat lubricant or additive.<sup>9-11</sup> Regarding the use of ILs as neat lubricants, several studies have shown great potential for this purpose.<sup>12-14</sup> But at present, using small quantity of ILs as additive, rather than in bulk as neat lubricants, for engine applications seems to be an economical option due to the higher cost of ILs. It should be noted, however, that the multiple-recycling of ILs after usage could diminish the overall cost of employing ILs<sup>15</sup> in actual applications. This is another cost effective aspect for investigation by the lubricant industry.

The early works were mainly focused on imidazolium cations based ILs.<sup>11</sup> The interest in phosphonium<sup>12</sup> based ILs has widely grown over the years in line with their increased commercial availability. They have been successfully tested for several applications. In this study, phosphonium cation and amide anion based ionic liquid was chosen as lubricant additive, and studied their different performance such as PPD, VI, anti-wear property in lube oil, as described in this article.

## **2.1.2. Experiments**

### **2.1.2.1. Materials**

Toluene, hydroquinone, and  $\text{H}_2\text{SO}_4$  were purchased from Merck Specialities Pvt. Ltd. Acrylic acid (GC Purity 99%) and decyl alcohol were obtained from Sisco Research Laboratories Pvt. Ltd. Ionic liquid  $[\text{P}_{6,6,6,14}]^+[\text{NTf}_2]^-$  namely Trihexyl tetradecyl phosphonium bis (trifluoromethyl sulfonyl) amide was purchased from sigma-aldrichpvt. ltd. and methanol was purchased from Thomas baker Pvt. Ltd. and were used as received. Benzoyl peroxide (BZP) obtained from LOBA chemical was recrystallized from  $\text{CHCl}_3$ -MeOH before use. Specifications of the chemicals are depicted in **Table 2.1**. Two different base oils (BO1 and BO2) were collected from IOCL, Dhakuria, Kolkata, India, and their physical properties are mentioned in **Table 2.2**.

### **2.1.2.2. Esterification and homopolymerisation of DA**

Esterification of acrylic acid with decyl alcohols, purification of the prepared esters and subsequent homo polymerization were carried out following the procedure as reported earlier publications from our laboratory,<sup>16</sup> also mentioned in chapter II of part I (Page No. 27-28).

### **2.1.2.3. Preparation of IL-Polymer blend**

Polymer-IL blends was prepared by mixing thedecyl acrylate (DA) polymer (P-1) with desired amount of IL (100 ppm, 300ppm, 500ppm with respect to the polymer) in a mechanical stirrer at 60<sup>0</sup>C for one hour. The blended sample was assigned as P-2 (for 100 ppm), P-3 (for 300 ppm) and P-4 (for 500 ppm). Four different concentrations (1-4% w/w) of additive (P-1 to P-4) doped base oils, namely BO1 and BO2 were prepared by the addition of required amount of sample to the base oils.

## **2.1.3. Measurements**

### **2.1.3.1. Spectroscopic measurements**

The IR spectra of the samples were recorded on a Perkin Elmer FT-IR 8300 spectrophotometer using 0.1 mm KBr cells at room temperature. The NMR spectra were recorded in a 300 MHz BrukerAvance FT-NMR spectrometer using 5mm BBO probe. CDCl<sub>3</sub> was used as solvent and tetramethylsilane (TMS) was used as reference material.

### **2.1.3.2. Thermogravetric test**

The thermograms in air were obtained on a Mettler TA-3000 system, at a heating rate of 10 K min<sup>-1</sup> at room temperature under atmospheric pressure taking 0.2 g of each polymer sample in a platinum crucible.

#### **2.1.3.3. Molecular weight determination by GPC**

The weight average and number average molecular weights ( $M_w$  and  $M_n$ ) and poly dispersity indices of the polymers were measured in Waters's GPC equipment using polystyrene standards for calibration in THF phase. Details of the experimental procedure followed were mentioned in an earlier publication.<sup>17</sup> The results are tabulated in **Table 2.3**.

#### **2.1.3.4. Pour point determination**

The pour point of the polymers in base oils was tested according to the ASTM D97-09 method on a Cloud and Pour Point Tester model WIL-471 (India).

#### **2.1.3.5. Viscosity index determination**

Kinematic viscosity (KV) of the polymer was determined separately at 40 °C and 100 °C by counting the time of flow of polymer solution in base oil using viscometer apparatus and measuring the density of it. According to ASTM D-7042 method and also by using the method of viscosity index calculation<sup>18</sup> the viscosity index of each polymer solution was determined.

#### **2.1.3.6. Shear stability determination**

Shear stability was determined of various concentrated solution of pure DA polymer, DA + Ionic liquid blending and Ionic liquid in lube oil. Tests and calculation were conducted as per ASTM D- 3945 and ASTM 6022 method.

#### **2.1.3.7. Anti-wear property determination**

Anti-wear (AW) properties of base stocks as well as additive doped base stocks were studied in sliding contact by means of a Four- Ball wear test Machine as per ASTM D-4172 method. The tests were carried out employing 20 kg and 40 kg load condition.

## 2.1.4. Results and discussion

### 2.1.4.1. Spectroscopic data

FT-IR spectrum (**Figure 1.15**),  $^1\text{H-NMR}$  (**Figure 1.16**) and  $^{13}\text{C-NMR}$  (**Figure 1.17**) spectra of poly (decyl acrylate) or homo polymer of decyl acrylate (HDA) are discussed in details in section B of Chapter I of Part I (Page No. 56-57).

IR spectra of ionic liquid + DA blends exhibited ester carbonyl stretching vibration at  $1715.14\text{ cm}^{-1}$  (**Figure 2.1**) which is less than that of HDA ester carbonyl stretching absorption ( $1732\text{ cm}^{-1}$ ). It is due to the fact that after blending some sort of attraction between oxygen lone pair of ester carbonyl group with the cationic part of ionic liquid occurred, which lessen the carbonyl absorption frequency.

### 2.1.4.2. Thermogravimetric analysis

Plot of TGA data in **Figure 2.2** presents a comparison between the thermal stability of homopolymer of DA and its blending with ionic liquid respectively. The analysis reveals that blending is thermally less stable than that of homopolymer.

### 2.1.4.3. Performance evaluation of the prepared polymers as PPD

The pour point (PP) values of the polymers in both the base oils are tabulated in **Table 2.4**, which indicates that their PPD efficiency increases (up to a certain limit) with increasing concentration of the polymer in base oils. Comparison among the PP values indicates that the efficiency of the polymers as PPD is greater for DA polymers than that of ionic liquid blend.

### 2.1.4.4. Photomicrographic analysis

The photo micrographs of lube oil (BO2) with and without different additives are shown in **Figure 2.3 (a–e)**. **Figure 2.3 a**, the photograph of the fresh lube oil showed large number of crystalline and some needle shaped wax crystals. But by the addition of polymers the wax crystal

size [Figure 2.3 (b-e)] is significantly decreased from large crystal structure (base oil) to very small dots dispersed in the oil phase of the lube oil, and the polymer which acts as better PPD (reveals by PPD data), decreases the wax size more compared to other. Therefore, a correlation between the depression of pour point and degree of wax structure modification has been confirmed.

#### **2.1.4.5. Performance evaluation of the prepared polymers as VMs**

The VI values in two base oils (measured in four different concentrations) tabulated in Table 2.4 indicates that in both the base oils the values for DA homopolymer are greater than that of its ionic liquid blend but the difference is small, Also the VI value decreases with increasing ionic liquid concentration in the blending feed. This result may be explained on the basis of the molecular weight of the polymers. Again, with increase in concentration of the polymers in solution, VI increases. The reason may be that although the viscosity of the lube oil gets decreased at higher temperature, the polymer molecules may effectively offset this reduction in viscosity by thickening the oil changing its shape from tight coil to expanded one due to increased polymer-solvent interaction. The result is increase in viscosity of the solution. Again, a higher polymer concentration means increase in total volume of polymer coils in the solution which imparts a higher VI compared to a low concentrated polymer solution.

#### **2.1.4.6. Shear stability analysis**

Shear stability determined on the basis of PVL (permanent viscosity loss) and PSSI (percent of shear stability index), lesser the value of PVL and PSSI greater the shear stability of the sample. Shear stability determination (Table 2.4) clearly indicates that IL+DA blend is more shear stable than that of DA polymer and also shear stability increases with the increasing the IL concentration in the blend feed. This result can be explained on the basis of the molecular

weights of the sample, higher the molecular weight greater the possibility of loss of shear stability of the polymer.

#### **2.1.4.7. Efficiency as anti-wear additive**

Anti-wear contributions of the additives are measured with respect to wear scar diameter (WSD) under two load conditions (20 kg, 40 kg). Effect of additive concentration on the anti-wear performance is also studied. Experiments are conducted at first with pure base oils followed by the additive doped base oils. The WSD measured in all these cases are depicted in **Table 2.5** and **Figure 2.4**. As expected, all the samples(P-1 to P-4) show better anti-wear performance compared to pure base oils and IL blend polymer(P-2 to P-4) are found to be more efficient than that of pure DA homopolymer (P-1). Also the performance increases with increasing the IL concentration in the blend feed. Irrespective of base oils or load condition, WSD decreases with increasing additive concentration. That is, both the additives are acting more efficiently at higher concentration level. Comparison between load conditions indicates that under milder condition (20 kg load), additives performance is found better (lower WSD value).

#### **2.1.5. Conclusions**

Evaluation of performance of the additives indicates that the DA homopolymer act as to some extent better PPD and viscosity modifiers compared to its ionic liquid blend, but, DA+ IL blend is more shear stable than that of DA homopolymer and shear stability increases with increasing the concentration of IL in blending feed. Investigation also indicates that IL blend polymers show more efficient anti-wear performance than that of DA homopolymer and the performance increases with increasing the concentration of IL in blending feed.

#### **2.1.6. References**

References are given in Bibliography under Chapter-II of Part-II (Page No. 195-197).

**Table 2.1. Specification of the chemicals used.**

<i>Chemical name</i>	<i>Source</i>	<i>Mole fraction purity</i>
Toluene	Merck Specialities Pvt. Ltd.	0.995
Hydroquinone	Merck Specialities Pvt. Ltd.	0.990
H <sub>2</sub> SO <sub>4</sub>	Merck Specialities Pvt. Ltd.	-
Acrylic acid	SRL Pvt. Ltd.	0.990
Decanol	S. D. Fine-Chem Ltd.	0.980
Hexane	S. D. Fine-Chem Ltd.	0.995
Methanol	Thomas Baker Pvt. Ltd.	0.980
Benzoyl peroxide	LOBA chemicals	0.980
[P <sub>6,6,6,14</sub> ][NTf <sub>2</sub> ]	Sigma-aldrich Pvt. Ltd.	-

**Table 2.2. Base oil properties.**

Properties	Base oils	
	BO1	BO2
Density at 313 K, kg.m <sup>-3</sup>	836.98	868.03
Viscosity at 313 K, Pa-s	5.97×10	20.31×10
Viscosity at 373 K, Pa-s	1.48×10	3.25 ×10
Cloud point, °C	-10	-8
Pour point, °C	-3	-6
Viscosity index	80	85

**Table 2.3. The weight average and number average molecular weights (M<sub>w</sub> and M<sub>n</sub>) and polydispersity of the sample**

sample	M <sub>n</sub>	M <sub>w</sub>	PDI
P-1	10152	14287	1.40
P-2	9885	14114	1.42
P-3	9662	14011	1.45
P-4	9278	13825	1.49

**Table 2.4. Tribological performance of the samples in two different base oil.**

sample	Conc. (%)	BO1				BO2			
		PP	VI	PVL	PSSI	PP	VI	PVL	PSSI
P-1	1	-6	95	0.432	8.978	-9	98	0.435	9.768
	2	-9	105	0.811	9.996	-12	110	0.832	10.778
	3	-12	115	1.353	12.411	-15	128	1.436	13.125
	4	-15	124	1.98	16.821	-18	138	2.112	17.835
P-2	1	-6	92	0.374	7.587	-9	95	0.382	8.421
	2	-6	99	0.644	8.456	-9	105	0.657	9.142
	3	-9	109	1.227	10.234	-12	121	1.259	11.247
	4	-12	119	1.59	15.527	-15	129	1.596	16.223
P-3	1	-6	91	0.298	7.214	-9	94	0.311	8.114
	2	-9	97	0.587	8.145	-12	101	0.59	8.985
	3	-9	105	1.14	9.857	-12	117	1.264	10.141
	4	-12	116	1.372	15.114	-15	123	1.415	15.784
P-4	1	-6	91	0.212	6.984	-9	93	0.242	7.128
	2	-9	95	0.478	8.11	-12	98	0.511	8.541
	3	-9	103	0.985	9.114	-12	113	1.1	9.886
	4	-12	111	1.154	14.954	-15	119	1.173	15.211

PP-Pour Point, VI-Viscosity Index, PVL-Permanent Viscosity Loss, PSSI-Percent of Shear Stability Index.

**Table 2.5. Anti-wear Performance of Additive Doped Base Oil**

sample	Base oil	WSD(mm) of additive-base oil blends								
		20 kg load					40 kg load			
		0%	1%	2%	3%	4%	1%	2%	3%	4%
P-1	BO1	0.981	0.976	0.967	0.952	0.931	0.978	0.974	0.965	0.939
	BO2	1.116	1.101	1.084	1.068	1.061	1.104	1.088	1.071	1.065
P-2	BO1	0.981	0.973	0.963	0.948	0.925	0.974	0.967	0.959	0.929
	BO2	1.116	1.085	1.068	1.054	1.047	1.095	1.079	1.065	1.054
P-3	BO1	0.981	0.967	0.957	0.941	0.919	0.969	0.962	0.952	0.922
	BO2	1.116	1.080	1.061	1.048	1.043	1.09	1.073	1.059	1.048
P-4	BO1	0.981	0.961	0.952	0.934	0.912	0.962	0.954	0.943	0.914
	BO2	1.116	1.072	1.054	1.04	1.033	1.081	1.064	1.05	1.041

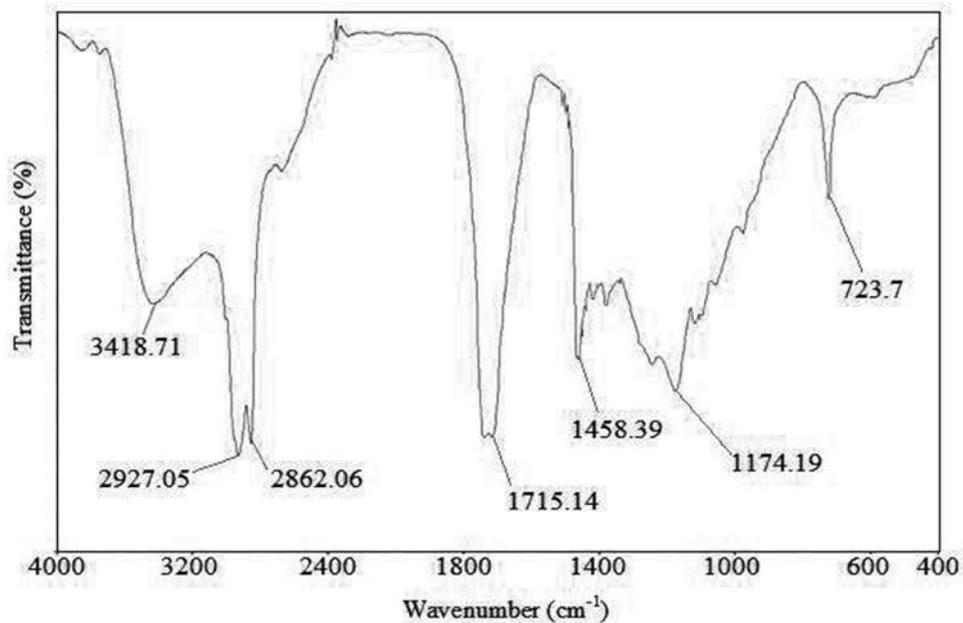


Figure 2.1. FT-IR spectra of Ionic liquid and poly (decyl acrylate) blend

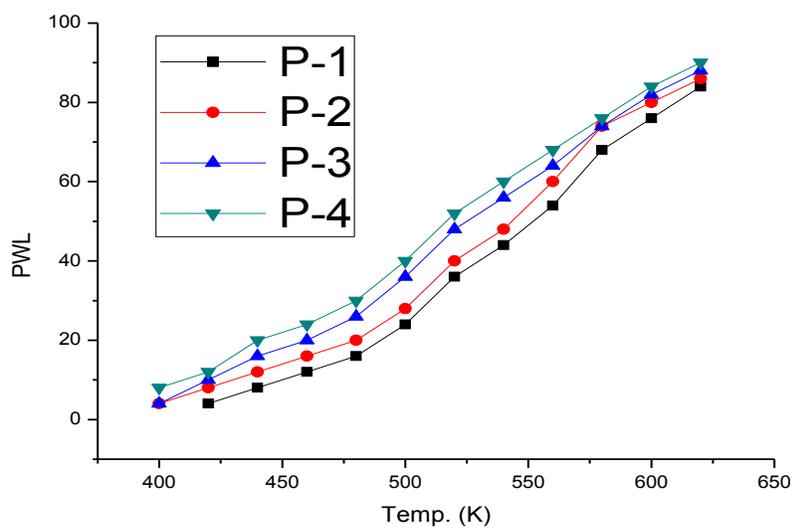
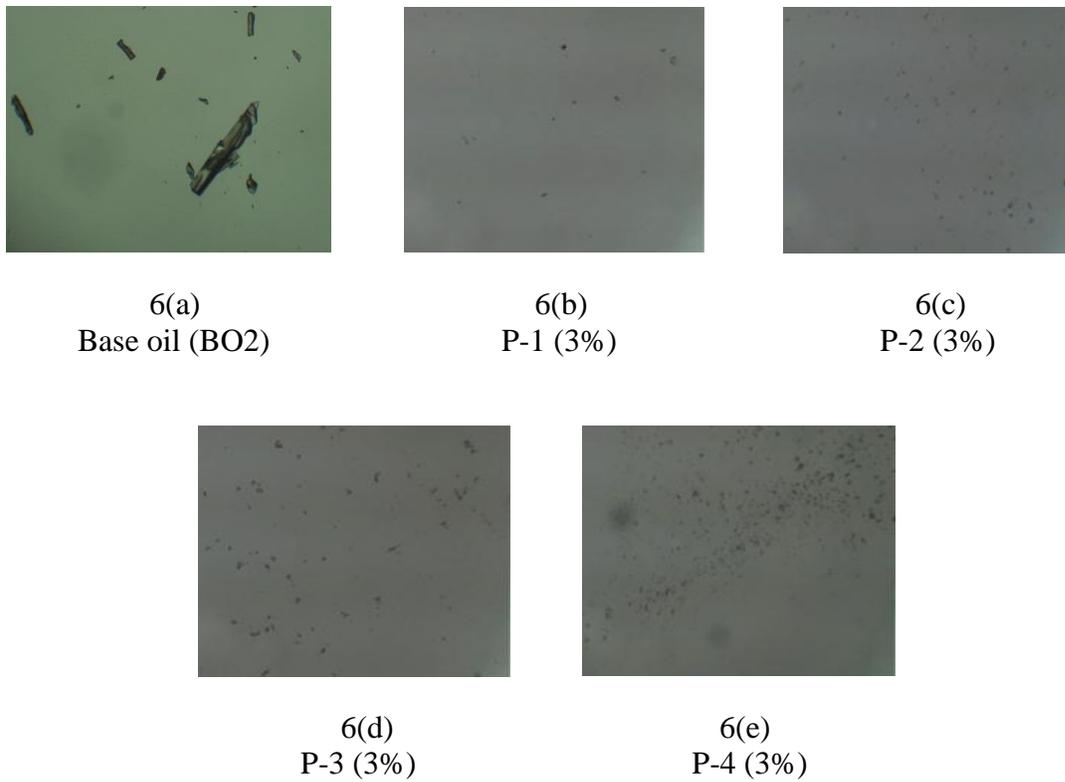
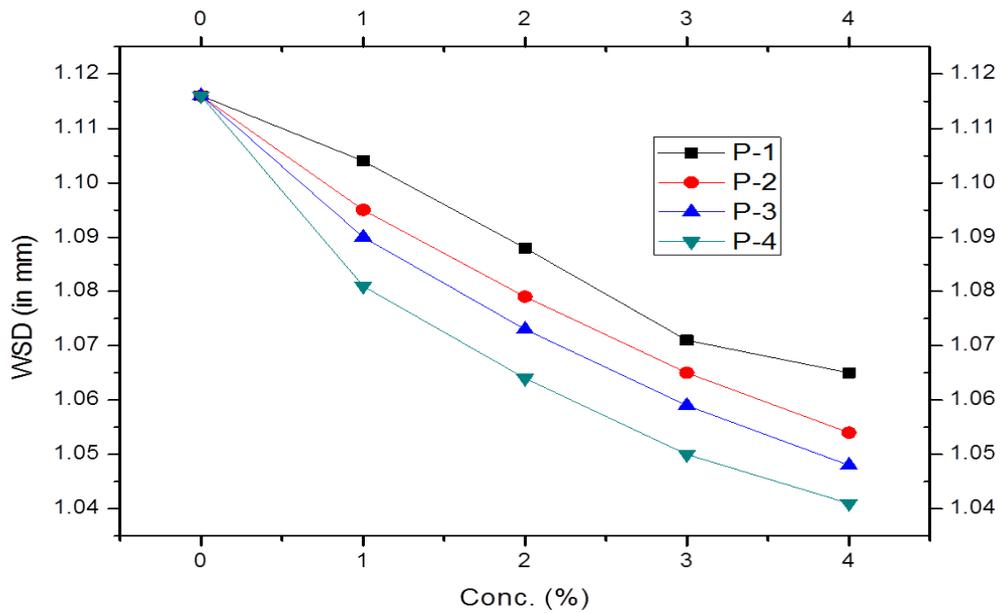


Figure 2.2. Plot of PWL (Percent Weight Loss) vs Temperature (in K)



**Figure 2.3(a-e). Plot of Photomicrographic images of base oil and additive (P-1, P-2, P-3 and P-4) doped base oil**



**Figure 2.4. Plot of WSD (Wear Scar Diameter) vs Concentration (%) of polymer in lube oil**