

CHAPTER IV

Ionic liquid doped polymeric additive

CHAPTER IV.A

An investigative approach towards the flow improvement property of ionic liquid doped polymeric additive in lubricating oil

IV.A.1. INTRODUCTION

Automotive industry is getting flourished day by day with new inventions and applications of lubrication science which is itself an ever exploring area of research. In general, a typical lubricant is composed of mineral base oils doped with different categories of additives such as antioxidants, detergents, dispersants, friction modifiers, pour point depressants (PPDs), antiwear additives, extreme–pressure additives, and viscosity modifiers as per requirement [1]. Recent advances with ionic liquids (ILs) have provoked a lot of studies on the application of ILs in the lubrication industry.

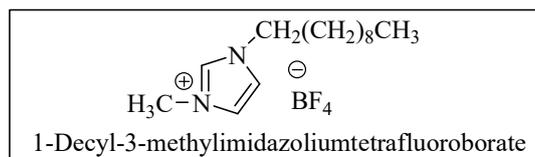
Ionic liquids are molten salts composed of large, asymmetric organic cations like imidazolium, ammonium, phosphonium etc and usually an inorganic anion such as tetrafluoroborate, hexafluorophosphate etc. The electrostatic force between the ions is highly diminished since the charges on the ions are usually diffuse over the large molecule and hence they fail to acquire a regular crystalline shape, rather they opt for the liquid state at room temperature mostly. ILs are unique to exhibit versatile properties such as low volatility, non–flammability, thermal stability, moisture stability, miscibility with organic compounds, good electronic and ionic conductivity and its broad application in electrochemical field [2]. They are often referred to as ‘designer solvents’ due to their ability to dissolve a variety of organic, inorganic and organometallic compounds by simply choosing the proper combination of cations and anions. In addition ILs are considered to be more environmentally friendly in comparison to current alternative solvents and electrolytes [3] and hence are treated as green solvents [4]. Most importantly, availability of various combinations of cation and anion enriched with unique properties, ILs have attained enormous attention over the decade [5] and today variety of ILs are explored with versatile application.

Such a promising range of properties along with their potential for controlled reactivity and also their low evaporation, researchers are provoked to explore their application in corrosion protection [6, 7] and tribology. Especially their extremely low vapor pressure, non flammability and thermal stability even upto temperatures above 200°C are accounting for their capability of lubricating even at increased temperatures and pressure.

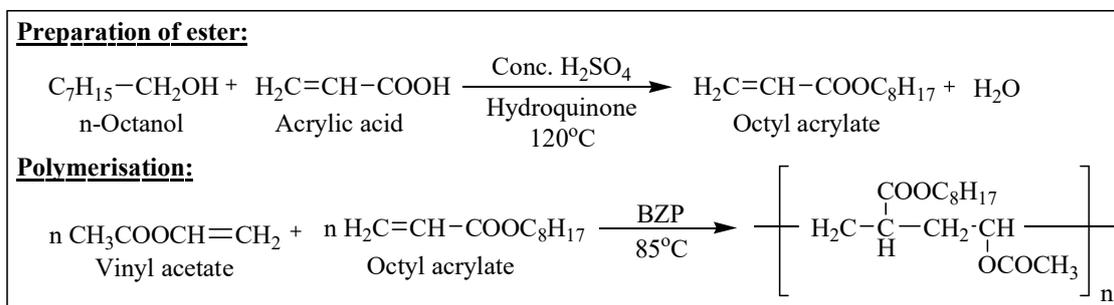
IV.A.2. BACKGROUND AND OBJECTIVES

Various studies have explored the versatile behavior of ILs in engine lubrication [8–11], micro–electromechanical machines (MEMs) [12–14], in the fully formulated diesel engine lubricants [15] etc. Phosphonium orthoborate ionic liquid was evaluated as a wear reducing additive in biodegradable oils at steel–steel surfaces in the boundary lubrication regime [16]. Tribological tests on 1,4–bis(2–ethylhexyl)sulfosuccinate anion–based ILs containing different cation–imidazolium and organoammonium revealed effective friction reduction and antiwear functionality [17]. Again phosphonate ionic liquids were used as additives in polyethylene glycol (PEG) for steel/steel contact by Yunyan Han et al. and their characterization showed that these ionic liquids improved the tribological performances of the base oil significantly [18]. Sulfate–based ionic liquid with a pyrrolidinium cation as neat lubricant and as additive for glycerol in lubrication of steel–steel contacts played an important role in the friction and wear reduction, as well as in the smoothening of the worn surface [19]. In other studies ILs were utilized in the mixed lubrication and the elastohydrodynamic lubrication regimes [20], in the possible base oil of next–generation space grease [21], in magnetic tapes [22] etc. Ammonium–based protic ionic liquids (PILs) showed that the increase of the anion carbon chain length in the PIL structure reduced significantly the coefficient of friction value [23]. Trihexyltetradecylphosphoniumbis(2–ethylhexyl)phosphate was evaluated as anti–wear additive which performed equally with the conventional anti–wear additive, zinc dialkyl–dithiophosphate (ZDDP) at room temperature and even at higher temperature 100°C the former outperformed the later [24]. Imidazolium–based ILs were utilized as additives in the base oil PEG to decrease the friction coefficient and improve the viscometric properties [25].

Imidazolium based ILs provide versatile application owing to their higher stability than a conventional synthetic oil at 200°C [26], easy adsorption onto a surface, such as phosphonyls and esters [27, 28] and easy variation of alkyl chain length to tune up wear and friction [29–32]. Imidazolium tetrafluoroborates are supposed to exhibit lower friction and wear than traditional lubricants for a number of systems [4, 33]. These immense applications of imidazolium tetrafluoroborates have initiated us to utilise it in our present work. But due to higher expense compared to mineral base oils and synthetic base oils, ILs cannot be used solely in large volume. But they may be used as a lubricant additive where a small amount of IL is doped into base oil [34]. To solve the solubility problem in non polar base oils [10, 35] longer alkyl chain is preferred as longer the alkyl chain length on the imidazolium group, higher is the solubility of IL in base oils [1]. Hence we opted for 1-decyl-3-methylimidazolium tetrafluoroborate for this present work.



Here we have prepared a copolymer of vinyl acetate and octyl acrylate and blended it with the said IL (**Scheme IV.A**). Vinyl acetate and acrylate-based polymers are broadly applicable to improve the flow ability of even very waxy crude oil, diesel fuel to other base oils at low temperature [36, 37].



Scheme IV.A: Preparation of octyl acrylate and its copolymerization with vinyl acetate

Vinyl acetate copolymers satisfy most of the properties, a good additive must possess. This reason actually prompted us to explore it in this present study where we have investigated the effect of the IL under consideration on the flow improvement properties of acetate–acrylate based copolymer.

IV.A.3. EXPERIMENTAL SECTION

IV.A.3.a. Materials

Octyl alcohol, Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), Acrylic acid were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme Ltd.) and Methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.) and Benzoyl peroxide (BZP, 98% Thomas Baker Pvt. Ltd.) were purified by recrystallization before use. Conc. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. The preferred IL 1–decyl–3–methylimidazolium tetrafluoroborate was obtained from TCI Chemicals (India) Pvt. Ltd. Properties of the mineral base oils used are mentioned in earlier Chapter II.A..

IV.A.3.b. Preparation of ester and its purification

The ester (octyl acrylate, OA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of octyl alcohol in presence of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone with respect to the total reactants as polymerization inhibitor and toluene as a solvent. The method of esterification and its purification were carried out by the process as reported in Chapter II.A [38].

IV.A.3.c. Preparation of polymer and its blend with IL

The copolymer of vinyl acetate and octyl acrylate was prepared by free radical polymerisation in presence of BZP as initiator (0.5% w/w, with respect to the total monomer) following the same process as described in Chapter II.A [38]. The prepared and purified copolymer was blended with the ionic liquid in 1:1 ratio via mechanical blending process in a magnetic stirrer at 60°C to obtain a homogeneous blend.

IV.A.4. MEASUREMENTS

IV.A.4.a. Molecular weight determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were determined by GPC method (Water 2414, polystyrene calibration) as described in Chapter II.A.

IV.A.4.b. Spectroscopic Measurements

Spectral data were obtained following the same procedure as in Chapter II.A.

IV.A.4.c. Performance evaluation as pour point depressants in base oil

The effect of additive concentration on pour point of the base oils was tested by using different doping concentrations ranging from 1% to 6% (w/w) for each of the prepared copolymer, IL and their blend. According to the ASTM D 97–09 method the pour points of the prepared solutions were measured using cloud and pour point tester model WIL–471 (India).

IV.A.4.d. Performance evaluation as viscosity index improver (VII)

According to ASTM D 2270–10 method viscometric parameters were determined at 313 and 373 K using different doping concentrations (% w/w) from 1% to 6% of the additives in the base oils. All of the experimental data, given in **Table IV.A.2 & IV.A.3** were noted by taking an average of three experimental results under identical conditions in each case.

IV.A.4.e. Shear stability measurement

Stability against mechanical shear is expressed in terms of shear stability index or PSSI values. It is basically measurement of viscosity loss under shearing condition which may be of two kinds such as Temporary Viscosity Loss (TVL) and Permanent Viscosity Loss (PVL) [39] discussed in **Chapter I** under section **I.A.1.b**. The PVL and PSSI values are measured for the solutions prepared using 1% – 6% (% w/w) doping concentration of the prepared copolymer, IL and their blend in the base oils as per ASTM D–3945 method and are given in **Table IV.A.4**.

IV.A.5. RESULTS AND DISCUSSION

IV.A.5.a. Molecular Weight Analysis

The obtained values of M_n , M_w and PDI of the prepared copolymer are 25339, 53374 and 2.11 respectively. In general, these values are kind of a proof for a successful polymerisation.

IV.A.5.b. Spectroscopic analysis

Spectral data with analysis of the prepared polymer have already been discussed in **Chapter II.A.**

IV.A.5.c. Performance evaluation as pour point depressant

Pour point data obtained from **Table IV.A.1** implies that the copolymer and its blend with IL are effective pour point depressant in both the base oils.

Table IV.A.1: Pour point data with respect to the different concentrations of the additives in base oil (BO)

Additive	BO	PP (°C) at different concentrations (% w/w) of additive						
		0%	1%	2%	3%	4%	5%	6%
Polymer	BO1	-3	-10.0	-10.9	-11.5	-11.9	-11.0	-10.5
	BO2	-6	-12.0	-12.5	-13.2	-12.9	-12.4	-11.9
IL	BO1	-3	-7.0	-7.5	-9.0	-8.4	-8.1	-7.0
	BO2	-6	-8.1	-9.3	-9.5	-10.2	-10.1	-10.1
Blend	BO1	-3	-10.7	-11.1	-11.7	-12.1	-11.9	-11.8
	BO2	-6	-12.4	-12.8	-13.3	-13.7	-13.6	-13.5

Concⁿ represents concentration in % w/w

High molecular weight of the polymer accounts for its effectiveness as pour point depressant. But the IL alone is hardly effective as PPD for the base oils. Since a polymeric backbone is a vital condition to be an effective pour point depressant the IL is lacking behind in this case. But due to the presence of a hydrophobic long alkyl chain which may interact with the wax coming out at reduced temperature from the base oil, a little change is observed in the pour point of the base oils. With increasing concentration the depression slightly enhances and gets fixed at some point due to lower solubility at higher concentrations as clearly shown in **Figure IV.A.1**. Better interaction is observed in case of the blend of the polymer and the IL. Comparing the data for the polymer and its blend with the IL, it is observed that they are more or less equally active as PPD, but the blend is slightly better which may be attributed to the fact that the IL under consideration also possessed a long alkyl chain which enhances the activity of the polymer.

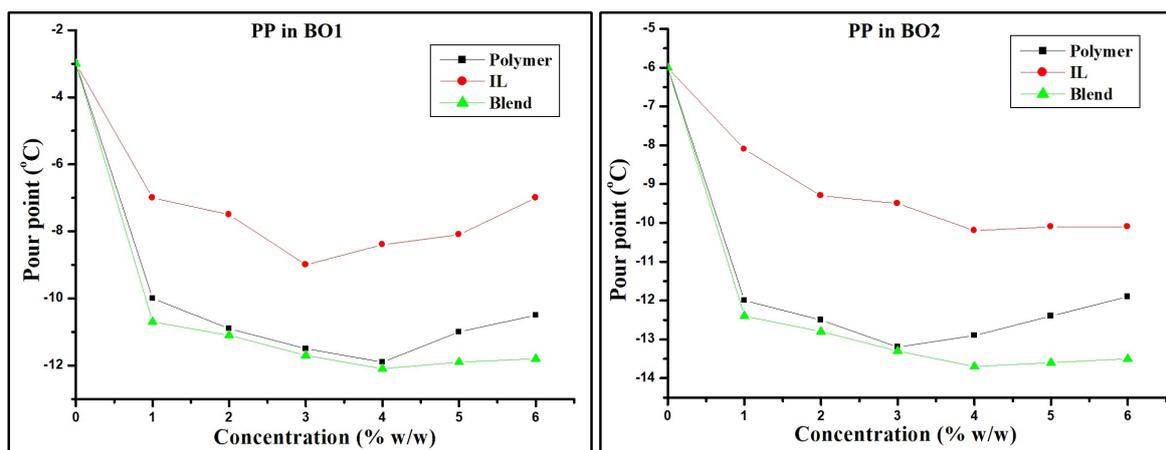


Figure IV.A.1: Variation of Pour point with respect to the different concentrations of the additives

IV.A.5.d. Performance evaluation as viscosity index improver

From the viscometric data (**Table IV.A.2 & IV.A.3**), it was observed that all the additives i.e. the copolymer, IL and their blend acted as moderate to good viscosity index improvers in both the base oils. If compared between IL and the copolymer of octyl acrylate and vinyl acetate, the later actually outweighs the IL. The obvious reason behind this is that the polymers exist as a coil in the base oil at normal temperature, but at elevated temperature this coil unfolds itself into a chain structure with higher volume and hence higher surface area that is responsible for higher

viscosity index of doped base oil. Thus temperature effect is reversed in case of polymers and as a result polymers act as better viscosity index improver in base oil.

Table IV.A.2: Viscosity Index (VI) data with respect to the different concentrations of the additives in base oil 1 (BO1)

Conc ⁿ	Polymer			IL			Blend		
	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI
1	6.705	2.120	113	6.700	2.033	86	6.721	2.181	135
2	6.714	2.160	127	6.706	2.051	91	6.737	2.223	147
3	6.727	2.200	141	6.712	2.072	98	6.763	2.274	162
4	6.750	2.250	157	6.720	2.094	104	6.792	2.325	176
5	6.780	2.300	170	6.729	2.125	113	6.822	2.355	184
6	6.810	2.340	184	6.738	2.143	118	6.841	2.391	197

Concⁿ represents concentration in % w/w; KV₁ & KV₂ represent kinematic viscosity at 40°C & 100°C respectively.

Table IV.A.3: Viscosity Index data with respect to the different concentrations of the additives in base oil 2 (BO2)

Conc ⁿ	Polymer			IL			Blend		
	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI
1	24.320	4.850	122	24.235	4.512	94	24.388	5.113	142
2	24.340	5.000	134	24.244	4.593	102	24.442	5.234	151
3	24.390	5.250	153	24.257	4.714	111	24.563	5.502	170

4	24.480	5.370	161	24.269	4.875	124	24.601	5.686	183
5	24.570	5.560	174	24.281	4.983	133	24.655	5.782	189
6	24.650	5.780	189	24.291	5.107	142	24.712	5.891	196

Concⁿ represents concentration in % w/w; KV₁ & KV₂ represent kinematic viscosity at 40°C & 100°C respectively.

Comparing all the data (Figure IV.A.2) it was observed that IL and the polymer blend acted as the best viscosity index improver among all three. It simply suggested that the IL under consideration actually enhanced the viscometric property of the polymer. The observation is not in any contrary to the other base oil also. Irrespective of all the additives and base oil, viscosity index gradually increased with increasing concentration of the additive which may be due to an increase in the total volume of the micelles in the oil solutions [40].

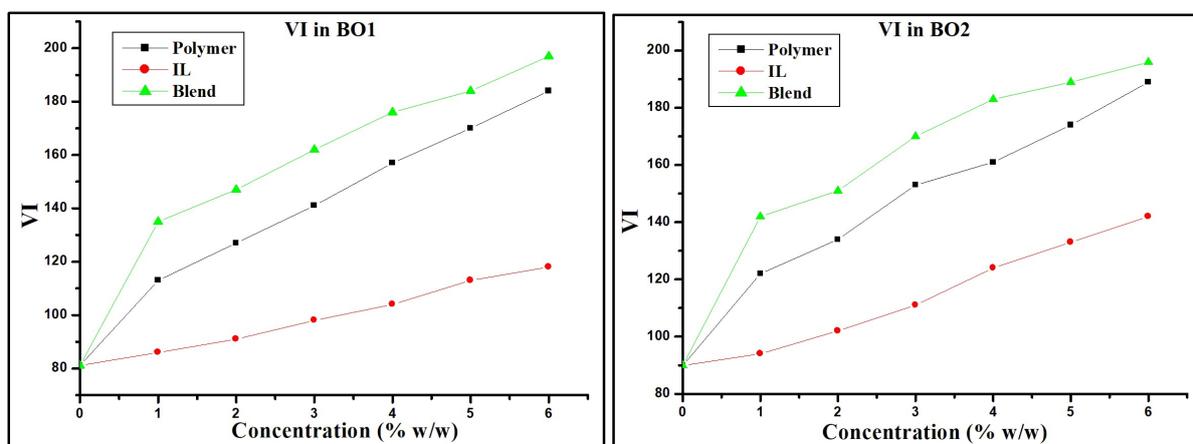


Figure IV.A.2: Variation of viscosity index with respect to the different concentrations of the additives

IV.A.5.e. Shear stability index analysis

The polymer–IL blend showed highest stability against mechanical shear at all concentrations, which clearly supports its better mechanical and thermal property in both the base oils (Table IV.A.4).

Table IV.A.4: PVL & PSSI data with respect to the different concentrations of the additives in base oil (BO)

Base Oil	Conc ⁿ	KV ₂ after shear			PVL (%)			PSSI (%)		
		Polymer	IL	Blend	Polymer	IL	Blend	Polymer	IL	Blend
BO1	1	2.081	2.022	2.142	1.84	0.54	1.79	39.00	84.61	24.22
	2	2.100	2.022	2.176	2.78	1.41	2.11	42.86	93.55	23.15
	3	2.120	2.031	2.215	3.64	1.98	2.59	44.44	78.85	23.23
	4	2.140	2.042	2.252	4.89	2.48	3.14	47.83	70.27	23.93
	5	2.150	2.047	2.271	6.52	3.67	3.57	53.57	74.28	25.07
	6	2.160	2.055	2.295	7.69	4.11	4.02	56.25	71.54	25.88
BO2	1	4.655	4.476	5.032	4.02	0.79	1.58	51.32	85.71	14.15
	2	4.710	4.492	5.137	5.80	2.19	1.85	54.72	82.11	12.69
	3	4.800	4.502	5.380	8.57	4.48	2.21	57.69	86.88	11.82
	4	4.837	4.528	5.545	9.93	7.12	2.48	59.22	85.68	12.84
	5	4.890	4.565	5.614	12.05	8.39	2.91	61.47	81.48	12.80
	6	4.930	4.635	5.709	14.71	9.24	3.09	64.89	74.09	12.81

Concⁿ represents concentration in % w/w; KV₂ represents kinematic viscosity at 100°C.

The PSSI data also suggested that the polymer is itself a good shear stable additive. But when blended with the IL under consideration, the mechanical stability is enhanced much more. It implies that the blend undergoes molecular degradation under mechanical shear at much lower rate compared to the polymer and the IL alone. Higher the concentration of the additive in the

base oil, higher is the volume exposed to the mechanical shear and hence the PSSI values increase with increasing concentration of the additive in both the base oils, but this relationship is not totally linear since some other factors also come into play under severe mechanical shear like molecular weight of the polymer, composition of the base oil etc.

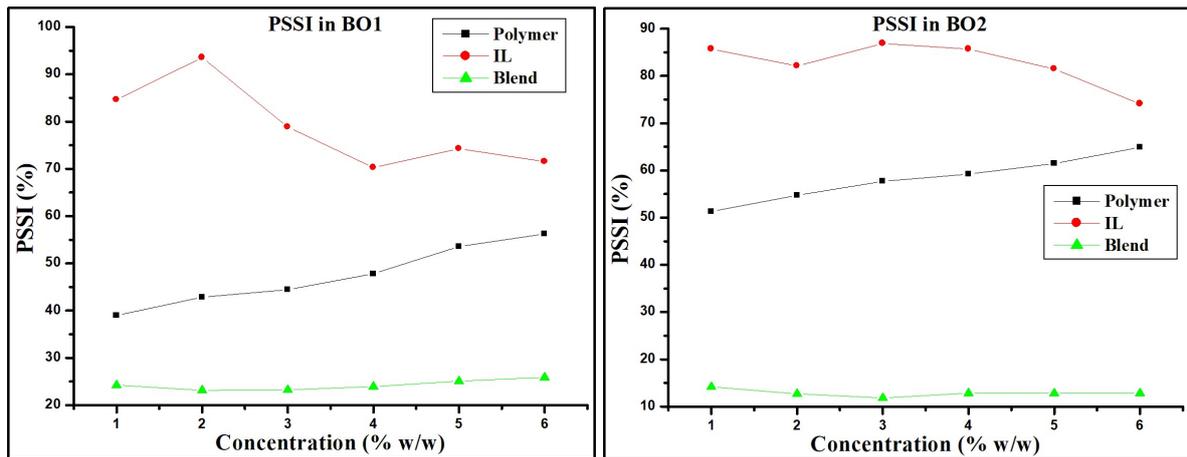


Figure IV.A.3: Variation of PSSI with respect to the different concentrations of the additives

Graphical representation (**Figure IV.A.3**) provides clear comparison of shear stability among the additives. It clearly shows that IL alone is comparatively poor shear stable than the polymer and the blend. The blend of the polymer and the IL here has been proved to possess better mechanical stability.

IV.A.6. CONCLUSION

From the above study, it may be concluded that the IL under consideration does play an effective role when blended with acetate–acrylate copolymer. The polymer is itself a good pour point depressant, viscosity index improver and at the same time it is quite stable against mechanical shear under severe condition. The IL alone is not as effective as the polymer in terms of pour point depressant, but its viscometric properties are moderate. Above all, blend of the polymer and the IL predominates in every property i.e. pour point depression, viscosity index and shear stability. Though IL has been proved to be a promising lubricating agent, its high cost retards its solo application. When blended with proper polymer, lower amount of IL is required which

lowers the cost to a considerable amount and at the same time the blend exhibits better property than even the parent polymer also.

IV.A.7: REFERENCES

References for chapter IV.A are given in bibliography section (page 137–140).

CHAPTER IV.B

Enhancement of additive properties in crude oil through introduction of ionic liquid

IV.B.1. INTRODUCTION

Crude oil, whether heavy, medium or lighter, is probably the biggest source of energy around the globe [1]. But crude oil extraction, transportation via pipeline or its storage require a lot of struggle basically due to its composition, high viscosity, high pour point and some other factors also. Crude oil is originally a form of unprocessed oil which is a complex mixture of hydrocarbons, particularly saturates, aromatics, resins and asphaltenes [2] and depending on the geological background, other heavy metal may be present in it [3]. At lower temperature n-paraffins precipitate out forming wax crystals and when the temperature decreases more, these crystals get bigger in size to form a 3-D network which finally immobilizes the oil. Thus transportation of crude via pipeline to the refineries or else becomes a hurdle at low temperature. High viscosity of crude oil is another barrier against its production and transportation as well since huge energy is required to dig out the oil from reservoir and the process gets worsened due to large pressure drop which in turn results in huge production loss [4]. Despite such drawbacks, heavy and even extra heavy crude oil is getting enough attention as the main energy source due to limited and decreasing source of medium or light oil. Hence petrochemical industry is exploring continuously new strategies to defeat the obstacles faced throughout the crude oil displacement from reservoir to production facilities and further into the refinery process up to conversion into various petrochemical products of higher commercial value [5].

To tackle these barriers, number of methods have been utilized viz. mechanical methods, thermal treatment, dilution of crude with light hydrocarbons, alcohols like pentanol, hexanol, etc, gasoline and middle distillates like kerosene [6] and chemical methods like treatment with surfactants, scavengers, emulsion breakers, polymers, nanoparticles and other chemical additives as wax modifier and viscosity reducer [7]. More or less all these processes come with their own drawbacks whether high cost in some cases or recovery of oil after treatment [8]. Application of

chemical additives like polymers have conquered much advanced place among these methods, but still it is a challenging area to find out a perfect multifunctional additive with maximum effect at minimum dosage.

Ionic liquids have emerged out as a promising candidate in this field with lots of potential. Basically ionic liquids are molten salts consisting of large, asymmetric organic cations like imidazolium, ammonium, phosphonium etc and usually an inorganic anion such as tetrafluoroborate, hexafluorophosphate etc. The most interesting feature of ILs is that variety of combination of cation and anion is available each with unique properties and hence versatile application of ILs is available in the industry [9]. ILs are enriched with low volatility, non-flammability, thermal stability, moisture stability, miscibility with organic compounds, good electronic and ionic conductivity which promoted its application in versatile studies such as in magnetic tapes [10], in electrochemical fields [11], in corrosion protection [12, 13], in engine lubrication [14] and micro-electromechanical machines (MEMs) [15–17]. Recently, many room temperatures ILs or RTILs are developed as potential “green” solvents due to their environment friendly and renewable characteristics [18]. Lots of studies have been performed promoting successful application of ILs in tribology [19–21]. Owing to high thermal stability, ionic liquids were investigated even as a possible base oil of next-generation space grease to solve mainly temperature related issues and compatibility with space environment [22].

IV.B.2. BACKGROUND AND OBJECTIVES

Due to such versatile applications, number of studies have been performed over the applicability of ILs in crude oil also, such as in enhanced oil recovery, asphaltene degradation, bitumen recovery, desulphurization, interfacial tension reduction in crude oil–water system etc [23, 24]. According to Nares et al. some ILs are capable of altering the viscosity of heavy crude [25]. ILs are well capable of preventing the precipitation of asphaltene during enhanced oil recovery (EOR) process by effectively breaking the asphaltene association [26]. Again some surface-active ILs can also be used as demulsification agents to break water/oil emulsion during oil refining process [27]. Sivabalan Sakthivel et al has investigated the enhancement of solubility of heavy crude oil in solvent and imidazolium-based IL mixture and reported almost 60% increase

in solubility compared to the blank solvent without IL [5]. According to their report, the ILs were successful in reducing the surface tension and interfacial tension between solvent and crude oil and hence this study provides an efficient pathway for the recovery of entrapped oil from exhausted reservoirs. Ali Alarbah et al. proved in their study with 1-ethyl-3-methyl-imidazolium acetate IL that the potential of injecting a slug of the IL and brine is much better than that of introducing a slug of alkali and brine in case of medium oil recovery [28]. Again, Mabkhot Bin Dahbag et al reported ammonium sulfate based IL as an efficient environment friendly substitute for surfactants in enhanced oil recovery (EOR) [29]. Another study by Zeeshan Rashid et al. suggested that ILs with hydrophobic anions can be used to prevent asphaltene deposition which is actually responsible for high viscosity of crude oil [30]. Imidazolium, pyridinium, and thiazolium based ILs were investigated as viscosity reducers for Mexican heavy oil and Canadian and Venezuelan bitumens by Deepa Subramanian et al and the study revealed that ILs with higher alkyl chain length at the cationic group are better viscosity reducer [31]. According to a study done by Watheq Kareem Salih, there is a clear relation between the molecular weight of ionic liquids and their efficiency in the demulsification process for crude oil emulsions viz. higher the molecular weight higher is the efficiency [32]. Thus ILs have lots of applications as viscosity reducer [33], surfactants [34] and demulsifiers [35] in petrochemical industry.

But ILs are comparatively much expensive than mineral base oils and synthetic base oils and hence they cannot be used solely in large volume. On the other hand, they may be used as a lubricant additive where a small amount of IL is doped into base oil to provide a large difference to the friction and wear [36]. In the present context, we have evaluated the performance of an imidazolium based IL in combination with acrylate-acetate copolymer in wax modification, viscosity modification and also evaluated their shear stability in crude oil. To tackle solubility issue we have opted for a long alkyl chain on the imidazolium group and since ILs having highly fluorinated anions possesses higher thermal stability, we preferred tetrafluoroborate as the anion part. On the other hand, vinyl acetate and acrylate-based polymers are broadly applicable to improve the flow ability of even very waxy crude oil, diesel fuel to other base oils at low temperature [37]. The aim of our present work is to find out whether the IL under consideration

can enhance the activity of the polymer when blended together in comparison of their solo application in crude oil. We have followed here the same scheme as we followed in the previous chapter (Chapter IV.A).

IV.B.3. EXPERIMENTAL SECTION

IV.B.3.a. Materials

Octyl alcohol, Acrylic acid, Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme Ltd.) and Methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.) and benzoyl peroxide (BZP, 98% Thomas Baker Pvt. Ltd.) were purified by re-crystallization before use. Conc. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. The crude oil was collected from IOCL, Assam having pour point of 27°C and densities of 0.851 and 0.808 g/cc at 40°C and 100°C respectively. The IL 1-decyl-3-methylimidazolium tetrafluoroborate was provided by TCI Chemicals (India) Pvt. Ltd. and was used as obtained.

IV.B.3.b. Preparation and purification of esters

The ester (octyl acrylate, OA) was prepared and purified following the same procedure as described in Chapter II.A.

IV.B.3.c. Preparation of copolymers and its blend with the IL

The copolymer of vinyl acetate (VA) and octyl acrylate (OA) was prepared by free radical polymerization in presence of BZP as initiator (0.5% w/w, with respect to the total monomer) following the same procedure as reported in Chapter II.A [38]. The prepared polymer was mixed with the IL in 1:1 ratio at a magnetic stirrer and heated at 60°C to obtain a homogeneous blend.

IV.B.4. MEASUREMENTS

IV.B.4.a. Molecular weight determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) of the prepared copolymer were measured by GPC method as described in Chapter II.A.

IV.B.4.b. Spectroscopic Measurements

Spectroscopic measurements were done as per the procedure mentioned in Chapter II.A.

IV.B.4.c. Performance evaluation as pour point depressants in crude oil

The effect of additive concentration on pour point of the crude oil was tested by using different doping concentrations ranging from 1% to 6% (% w/w) for the prepared copolymer, IL and their blend separately. According to the ASTM D 97–09 method the pour points of the prepared solutions were measured using cloud and pour point tester model WIL–471 (India). The obtained result is given in **Table IV.B.1**.

IV.B.4.d. Performance evaluation as viscosity index improver (VII)

Viscometric parameters were determined according to ASTM D 2270–10. The kinematic viscosity of the crude oil containing the copolymers and the blend was determined at 40°C and 100°C. Different concentrations of the polymers in the crude (% w/w) from 1% to 6% were used to study the effect of concentration on VI of the additive–doped crude oil. All of the experimental data, given in **Table IV.B.2** were noted by taking an average of three experimental results under identical conditions in each case.

IV.B.4.e. Shear stability measurement

Under severe mechanical stress an additive experiences molecular degradation and hence loses its activity as a VII. The more the degradation the more will be activity loss. Thus mechanical stability against shearing condition is measured in terms of shear stability index which is discussed earlier in **Chapter I** under section **I.A.1.b**. The PVL and PSSI values are measured here

preparing 1%–6% solutions (% w/w) of the prepared copolymers and their blend in the crude oil as per ASTM D–3945 method and are given in **Table IV.B.3**.

IV.B.5. RESULTS AND DISCUSSION

IV.B.5.a. Molecular Weight Analysis

Molecular weight is one of the key indicators of a proper polymerization process. The prepared copolymer exhibited number average molecular weight of 25339 and weight average molecular weight of 53374 in GPC. Such high value of molecular weight is very helpful towards its application as PPD or VII. Besides its PDI value was 2.11 which imply that the copolymer is highly polydispersed.

IV.B.5.b. Spectroscopic analysis

Spectral data with analysis of the prepared polymer have already been discussed in **Chapter II.A**.

IV.B.5.c. Performance evaluation as pour point depressant

It is evident from various studies that polymers with higher alkyl chain length are more effective flow improver [40]. Our prepared copolymer of octyl acrylate and vinyl acetate has been proved to be no exception in this case. From the pour point data (**Table IV.B.1**), it has been seen that this copolymer is really an effective PPD for the crude oil under consideration.

The graphical representation (**Figure IV.B.1**) cites the result better where a sharp decrease in pour point of the crude oil is observed when the polymeric additive was added. But the IL alone has hardly any effect on the pour point of the crude oil. A little variation in pour point of the crude is observed when doped with IL alone which is indicative for some possible interaction between the long alkyl chain on the imidazolium group and the paraffin waxes of the crude.

Table IV.B.1: Pour point data (°C) with respect to the different concentrations (% w/w) of the additives in crude oil

concentration	Polymer	IL	Blend
0%	27	27	27
1%	6.5	24.0	5.8
2%	6.2	22.6	5.5
3%	5.7	22.0	5.1
4%	4.9	22.3	4.5
5%	4.4	23.0	4.2
6%	4.4	23.6	4.3

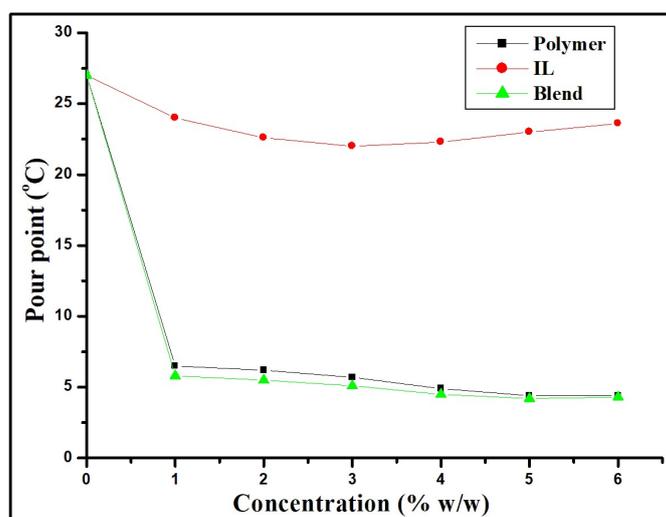


Figure IV.B.1: Variation of pour point with respect to the different concentrations of the additives

The blend of the copolymer and the IL virtually predominates over others as PPD. It simply suggests that the IL actually enhances the effectiveness of the copolymer. Presence of acrylate and acetate groups in the polymer makes it really active to interact with the IL which itself is unique to possess a complex mixture of interactions like ionic interaction, covalent

interaction, van der Waals interaction and even hydrogen bonding. At higher doping concentrations of the additives in the crude oil, the pour point just ceased to change due to less solubility which clearly supports the fact that the effectiveness of PPDs depends very much on their solubility.

IV.B.5.d. Performance evaluation as viscosity index improver

Asphaltene aggregation is a major factor for high viscosity of crude oil [41]. Besides presence of strong bonds like C=S drastically increases the viscosity of the crude [42]. Hence any interaction with the asphaltenes via pi-pi, aliphatic, acid-base, or charge-transfer interactions may result in viscosity change. Ionic liquids are well capable of exhibiting aromatic, aliphatic, acid-base, and charge-transfer interactions [43]. It may be mentioned here that the measured kinematic viscosities at 40°C and 100°C of the untreated crude oil under consideration are 11.243 and 2.926 cSt respectively.

Table IV.B.2: Viscosity Index (VI) data with respect to the different concentrations of the additives in crude oil

Conc ⁿ	Polymer			IL			Blend		
	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI
1	5.953	2.217	233	5.532	2.112	235	5.413	2.091	243
2	5.861	2.230	239	5.465	2.105	241	5.327	2.087	250
3	5.673	2.193	262	5.343	2.093	252	5.234	2.065	258
4	5.513	2.176	280	5.217	2.072	263	5.148	2.054	267
5	5.507	2.171	278	5.112	2.051	272	5.033	2.027	275
6	5.504	2.167	276	5.021	2.034	281	4.934	2.013	284

Concⁿ represents concentration in % w/w; KV₁ & KV₂ represent kinematic viscosity at 40°C & 100°C respectively.

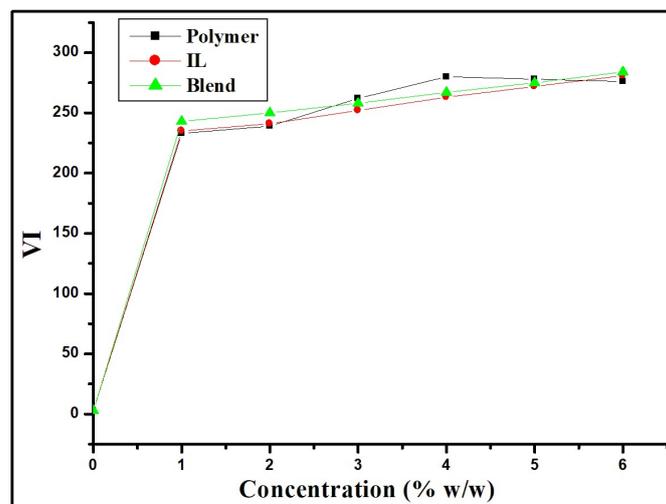


Figure IV.B.2: Variation of viscosity index with respect to the different concentrations of the additives

From the viscometric data obtained from **Table IV.B.2**, it is obvious that our chosen IL is really an effective viscosity reducer for the crude oil. Asphaltenes are reported to be strong H-bond receivers and ILs have the capability to act as strong H-bond donor [30]. Hence ILs can act as asphaltene stabilizer. Besides dispersing properties of ionic liquids along with solvating properties make them suitable candidate for treating asphaltene rich crude oil. Our chosen IL fulfills all the criteria required for possible interaction with asphaltenes and also with the paraffins of the crude oil. Presence of long alkyl chain on the imidazolium group accounts for some aliphatic interaction as well along with other interactions. In case of doping with the copolymer also, definite viscosity reduction is observed though comparatively little but distinct. Presence of acrylate and acetate functionality in the polymer may be the reason behind some interaction to reduce viscosity. But dramatic reduction is observed when doped with the copolymer-IL blend. The result is better represented in **Figure IV.B.2**.

With increasing concentration of the additive in the crude oil viscosity index has been increased, but at higher concentrations this change has almost vanished due to lower solubility which means solubility of the additive does play an important role for viscosity modification. Another noticeable thing is that at 40°C the effect of the additives in reduction of kinematic

viscosity is prominent, but at 100°C the effect is very little since at this higher temperature the viscosity the untreated crude oil itself is highly diminished.

IV.B.5.e. Shear stability index analysis

Shear stability index is an important parameter for a multifunctional additive since from production to refining a crude oil has to undergo a lot of processing stages which may involve severe mechanical shear also. To maintain the activity, an appropriate multifunctional additive for the crude oil must be shear stable also. In this view our obtained result is really an optimistic one.

Table IV.B.3: PVL & PSSI data with respect to the different concentrations of the additives in crude oil

Conc ⁿ	KV ₂ after shear			PVL (%)			PSSI (%)		
	Polymer	IL	Blend	Polymer	IL	Blend	Polymer	IL	Blend
1	2.475	2.217	2.156	11.64	4.97	3.11	36.39	12.90	7.78
2	2.481	2.211	2.152	12.62	5.04	3.11	38.45	12.91	7.75
3	2.486	2.207	2.147	13.36	5.45	3.97	39.97	13.69	9.52
4	2.487	2.203	2.143	14.29	6.32	4.33	41.47	15.34	10.21
5	2.518	2.198	2.140	15.98	7.17	5.57	45.96	16.80	12.57
6	2.534	2.193	2.136	16.94	7.17	5.95	48.35	17.83	13.19

Concⁿ represents concentration in % w/w; KV₂ represents kinematic viscosity at 100°C.

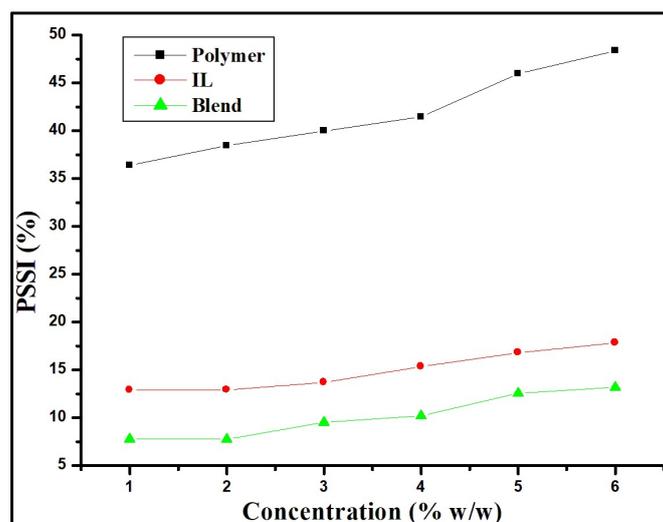


Figure IV.B.3: Variation of PSSI with respect to the different concentrations of the additives

Analyzing all the data (**Table IV.B.3**) it may be said the copolymer and the blend are very much shear stable in the crude oil under consideration. In case when the crude oil is treated with the IL alone, change in viscosity after shear is high which implies that the IL undergoes molecular degradation fast under mechanical shear which is better represented in **Figure IV.B.3**. In case of the polymer doped crude oil viscosity change is low. Most interesting result has been obtained in case of the blend. The result clearly showed that this blend of the copolymer and the IL is comparatively much more resistant against degradation under mechanical shear. When blended together there has been arisen number of possible interaction between to copolymer and the IL due to presence of variety of functionality in both the system and thus a better mechanically stable system of blend has been obtained. Again effect of concentration also has played an important role. With increasing concentration of the additive PSSI value increases, but not linearly since some other factors also may have a role here.

IV.B.6. CONCLUSION

In summary it may be said that an imidazolium-based IL doped polymeric additive has been developed which has been proved to be a better pour point depressant, a good viscosity reducer of asphaltene rich crude oil and at the same time possessed better shear stability in comparison to its parent copolymer and the IL. It was evident that the IL under consideration actually promoted

the activity of the copolymer which is itself a good PPD and VII. The IL had the capability to interact well with the asphaltene of the crude oil and hence could play an efficient viscosity reducer. This study provides a way to explore ionic liquids in enhancement of performance of polymeric additives. Since solo application of IL is a costly one, this doping method where little amount of IL is required, a cost effective approach has also been developed here for treatment of crude oil.

IV.B.7: REFERENCES

References for chapter IV.B are given in bibliography section (page 141–144).