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## Evaluating the Effectiveness of newly prepared Asymmetric Dicationic Ionic Liquids in Egyptian Base Oil improvement II

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#### ABSTRACT

This study synthesized three types of asymmetric dicationic ionic liquids, specifically, 1-(2-(1-decyl-1*H*-imidazolium-3-yl) ethyl)-3-methylpyridinium bromide (IL<sub>201</sub>), 1-(5-(1-decyl-1*H*-imidazolium-3-yl) pentyl)-3-methylpyridinium bromide (IL<sub>202</sub>), and 1-(10-(1-decyl-1*H*-imidazolium-3-yl) decyl)-3-methylpyridinium bromide (IL<sub>203</sub>) and evaluated their structures via elemental analysis, FT-IR, and <sup>1</sup>H-NMR spectroscopy also their surface activity, (surface tensions, critical micelle concentration, effectiveness, maximum surface excess and minimum surface area), were studied. Their influence on base oil was evaluated, including foaming characteristics and oxidation stability by studying the change in total acid number 'TAN' and viscosity. IL<sub>203</sub> was found to be the most efficient base oil improver, followed by IL<sub>202</sub> and IL<sub>201</sub>.

## **Key Words:**

Ionic liquid, Surface parameters, Base oil, Oxidation stability, Total acid number, Foaming, Spectroscopy

## 1. INTRODUCTION

One of the key end products produced from crude oil is vehicle lubricating base oil [1]. Lubricating base oil serves as a vital component in various industries, such as automotive, aviation, marine, and industrial machinery. The production of lubricating base oil from crude oil involves extraction through drilling, followed by distillation and purification through solvent extraction and dewaxing processes to remove impurities and unwanted components. There are different types of lubricating mineral-base oils produced from crude oil, paraffinic and naphthenic based lubricating oils [2].

Lubricant additives effectively improve the performance of base oils and are considered important components in the lubricant formulation process. Additives are added to the base oil to enhance its ability to lubricate and protect the machinery by reducing wear. Additives can be classified into different types based on their ability to improve the quality and lifespan of base oil. The first group gives the base oil new features and includes surface protective additives, such as detergents, corrosion inhibitors,

dispersants, extreme pressure additives, and anti-wear additives. The second group of additives works to enhance the existing properties of base oil and includes performance additives, such as viscosity index improvers, friction modifiers, and pour point depressants. The third group is lubricant protective additives, it takes care of changes that happen to the lubricant oil during its service life such as antifoaming and antioxidant agents [3]. Some additives such as detergents and dispersants are used to keep the machinery clean by preventing the formation and accumulation of deposits and sludge. Additionally, the anti-wear agents protect the engine from wear and tear. Antioxidants protect the oil from oxidation and degradation. Also; friction modifiers are used to reduce friction and hence improve fuel economy, the viscosity index improvers are used to improve the viscosity-temperature relationship of the base oil, and antifoaming stops the lubricant foaming and collapses the foam when formed due to entrain of air or gases into the oil.

Owing to the variety of applications for lubricants, different types of additives, (base oil improvers) are required [4]. Lubricants consist of a base oil along with several additional substances (additives) that modify and improve their properties and performance. The selection process of base oils and additives are critical to achieving optimum lubricating oil performance and depends on the specific requirements of the machinery and application, It is important to ensure that the additives used are compatible with the base oil to prevent any adverse effects or performance issues [3].

Lubricants play a crucial role in maintaining the smooth operation of machines and engines. Adequate lubrication can help to reduce friction, wear, and tear on the moving parts, prolonging the lifespan and improving its performance [5]. High-performance lubricants are particularly important in meeting the growing need for machines to operate under extreme conditions, such as high temperatures and pressures, while still achieving the lubrication goal [6]. Moreover, recent research has placed a greater emphasis on developing environment-friendly lubricants [7] with reduced side effects such as varnish formation and corrosion-related issues [8][9]. This is because lubricant-related downtime can result in significant losses from a lack of production [10]. Traditional lubricant oils have limitations in terms of their performance under extreme conditions compared with modern lubricant oils [11]. As a result, there has been a great deal of research into new and innovative lubricant oils that can meet the demands of modern industry by achieving operational, economic, and environmental gains [10]. One such area of research is the use of ionic liquids as lubricant base oils and lubricant oil improvers [11]–[13]. Moreover, the use of ionic liquids as lubricant base oil can have a positive impact on the environment. Traditional lubricant base oils are often derived from non-renewable resources and are not biodegradable [14], leading to environmental pollution. In contrast, ionic liquids base oils are generally considered to be more environmentally friendly due to their biodegradability [15].

Ionic liquids are salts that exist in a liquid state, even at or near room temperature. They possess unique physicochemical characteristics that make them attractive for a variety of applications [16], including as lubricant oil improvers [15]. One class of ionic liquid that has emerged as a promising candidate for lubricant base oil improvement is dicationic ionic liquids [17]–[20]. Dicationic ionic liquids are composed of two charged cations and two counter anions, which gives them a higher degree of complexity and exhibit superior physical properties compared to mono ionic liquids. The unique properties of dicationic ionic liquids make them particularly well-suited for lubricant oil additives. They have high thermal stability, low volatility, lower critical micelle concentration (CMC) in their aqueous solutions, excellent lubricity [21], and can be tailored to meet specific performance requirements [22][23]. Because they are ionic, they are less prone to evaporation and can provide long-lasting lubrication. One of the factors that contribute to the superior lubrication properties of dicationic ionic liquids librication even under extreme pressure conditions [25]. Additionally, researchers investigated the tribological properties of a dicationic ionic liquid as a lubricant additive in a steel-steel contact. The results showed that the dicationic ionic liquid exhibited low friction coefficients

and was able to significantly reduce friction and wear thus enhancing their lubrication properties compared to a traditional lubricant [12], [18].

The use of dicationic ionic liquids is not without its challenges, however one issue is their relatively high cost compared to traditional lubricant base oils additives [5], [26] which may limit their widespread use. Although using dicationic ionic liquids as lubricant oils carries several challenges, the potential benefits are significant enough to warrant serious consideration for practical applications. By providing superior performance under extreme conditions, they can help to reduce maintenance costs, reduce the need for frequent oil changes, increase efficiency, and prolong the lifespan of machines [5], [27] hence minimizing the operational cost. In conclusion, the use of dicationic ionic liquids as lubricant base oil improvement is an exciting and promising area of research. With their unique physicochemical properties, dicationic ionic liquids offer a range of benefits that could lead to significant advancements in lubricant technology. While there are still challenges to overcome, the potential benefits of using dicationic ionic liquids as lubricant base oils make them a promising candidate for a wide range of applications. Future research in this area will likely focus on optimizing the performance of dicationic ionic liquids through modifications to their chemical structure, as well as improving their synthesis and reducing their cost. With continued development, it is possible that dicationic ionic liquids could become a standard lubricant base oil in the near future.

## 2. STUDY AREA

In our previous work we synthesized and studied different heterocyclic compounds, [28]–[34], azo-phenols, [35], azo-liquid crystals, [36]–[38], for base oil improvement such as antioxidants, viscosity improvers and pour point depressants. This paper is part of a series of research that focuses on the synthesis and evaluation of dicationic ionic liquids, specifically as base oil improvers [20]. In this present work we synthesized and studied the effect of some asymmetric dicationic ionic liquids as antioxidants, viscosity improvers and anti-foaming agent for tested Egyptian hydro-finished base stock.

## 3. MATERIALS AND METHODS

**3.1 Samples collection and analysis:** Studied base oil was delivered from Co-operation Petroleum Company Egypt. The physicochemical characteristics were measured according to the American Society of Testing and Materials (ASTM) Table 1.

Test	Result	Standard Test Method
Density @ 15.56 °C, g /cm <sup>3</sup>	0.8807	ASTM D1298
Pour Point, °C	0	ASTM D97
Viscosity @ 40 °C	165.33	ASTM D445
@ 100 °C	15.56	
Viscosity Index (VI)	95	ASTM D2270
Total Acid Number (TAN)	0.061	ASTM D664
Foaming Characteristics at 50°C,	170	4 STM D802
Foaming Volume (ml)	480	A51W1D672
Sulfur Content, (wt.%)	0.41	ASTM D4294
Color	3.5	ASTM D1500
Copper Corrosion	1a	ASTM D130
Flash Point, °C	220	ASTM D92
Ash Content, (wt.%)	0.003	ASTM D482

Wax Content, wt.%	1.6	UOP 46
Saturate Content, wt.%	54.36	
Aromatic Content, wt.%	45.54	
Molecular weight	321.23	

#### Table1: Physicochemical properties of base oil

3.2 Synthesis of 1-(n-(1-decyl-1*H*-imidazol-3-ium-3-yl) alkyl)-3-methylpyridin-1-ium bromide ionic liquids compounds: Chemicals and solvents were purchased from international chemical companies and were used without further purification. Acetonitrile (anhydrous), ethyl acetate (99.5%), absolute ethyl alcohol, 1*H*-imidazole (99%), petroleum ether (40–60) (98%), and potassium hydroxide (97%), Merck. 3-Methyl pyridine (99%), 1,2-dibromoethane (99%), 1,5-dibromopentane (99%), 1,10-dibromodecane (99%), and 1-bromodecane Alfa Aesar. Steps of synthesis were illustrated as follows:

I-decylimidazole was prepared previously [39]. In a conical flask, 1*H*-imidazole (0.1 mol) and potassium hydroxide (0.1 mol) were dissolved in acetonitrile (50 ml) with stirring at room temperature. 1-Bromodecane (0.11 mol) was added dropwise for 1h. Stirring is continued till a white precipitate of potassium bromide is formed. The precipitate was eliminated by filtration and the filtrate is evaporated under vacuum. The product is washed several times with ethyl acetate, to remove the excess reactants, and evaporated under vacuum; Equation 1.



Eq 1: Preparation of 1-decyl-1*H*-imidazole





Compounds 201, 202 and 203 were prepared by stirring 3-methyl pyridine (0.01 mol) and dibromo alkanes, (1,2-dibomoethane, 1,5-dibromopentane and 1,10-dibromodecane) (0.015 mol) at room temperature for 24 hrs. The mixtures were washed several times with ethyl acetate to remove unreacted reactants. The white precipitate was filtrated and recrystallized from petroleum ether 40–60; Equation 2 [40].



Eq 2: Preparation of 1-(n-bromoalkyl)-3-methylpyridin-1-ium bromide

201; n = 2, 1-(2-bromoethyl)-3-methylpyridin-1-ium bromide

202; n = 5, 1-(5-bromopentyl)-3-methylpyridin-1-ium bromide

203; n =10, 1-(10-bromodecyl)-3-methylpyridin-1-ium bromide

Mechanism of reaction:



Synthesis of Ionic Liquids IL<sub>201-203</sub>: These compounds were synthesized by refluxing 1*H*-decylimidazole (0.01 mol.) with compounds 201-203, (0.01 mol.) in 50 ml acetonitrile for 12 hrs at 80 °C. Purification of the products was carried out via evaporation of acetonitrile under vacuum; Equation 3, [41].



#### Eq 3: Preparation of IL<sub>201-203</sub>

IL<sub>201</sub>: 1-(2-(1-decyl-1H-imidazol-3-ium-3-yl) ethyl)-3-methylpyridin-1-ium bromide.

IL<sub>202</sub>: 1-(5-(1-decyl-1*H*-imidazol-3-ium-3-yl) pentyl)-3-methylpyridin-1-ium bromide.

IL<sub>203</sub>: 1-(10-(1-decyl-1*H*-imidazol-3-ium-3-yl) decyl)-3-methylpyridin-1-ium bromide.

Mechanism of reaction:



The synthesized compounds were characterized using the conventional tools of analysis, Elemental analysis (Elementary Viro El Microanalysis), FT-IR spectrophotometer (Model 960 Mooog, ATI Mattson Infinity Series) and <sup>1</sup>H-NMR spectra (Bruker High-Performance Digital <sup>1</sup>H-NMR Spectrometer Advance III 400 MHz) using DMSO as solvent.

**3.3 Surface tension measurements:** Surface tension measurements were carried out using a Du Noüy tensiometer with a platinum ring. Freshly prepared aqueous solutions of  $IL_{201-203}$  were determined over a concentration range of 0.01–0.000001 M/L at 25°C. The instrument was calibrated using the value of surface tension of double distilled water, which was generally 72:00 ± 0:50 mN/m. Every sample solution was prepared with the double distilled water which was stabilized for 5 min in the instrument before measurements and was repeated three times to reduce the error [42], [43].

**3.4 Total Acid Number (TAN):** Total acid number was determined for the base oil before and after the addition of the three prepared compounds according to ASTM D664 [44] using Metrohm Titrando 905 potentiometer, stirrer 801 and electrode model 6.0229.010. Instrument parameters were used according to Metrohm Application Bulletin AB-404/2e.

**3.5 Viscosity:** Kinematic viscosity was determined, (ASTM D445) [45], viscosities of the base oil before and after the addition of the three  $IL_{201-203}$  were determined using CT-1000 CANON oil bath, Cannon- Fenske viscometers size 150, and Kohler thermometer instrument.

**3.6 Foaming characteristics** were determined, (ASTM D892) [46] for base oil before and after the addition of  $IL_{201-203}$ , using Petrotest DP water bath and ZEAL DM3A gas meter.

## 4. RESULTS AND DISCUSSION

## **Physico-chemical parameters**

- 4.1 Characterization of IL<sub>201-203</sub>:
- *Elemental analysis*; The tabulated data (Table 2) revealed that the calculated values are in good match with the observed ones.

IL	C%		Н%		N%		Br%		Mol.	Yield	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Wt.	%	
IL <sub>201</sub>	51.55	51.22	7.21	7.18	8.59	8.65	32.66	32.94	489	78	
IL <sub>202</sub>	54.24	54.08	7.78	7.82	7.91	7.87	30.07	30.24	531	75	
IL <sub>203</sub>	57.90	57.95	8.55	8.48	6.99	7.08	26.57	26.48	601	81	

## Table 2: Elemental analysis of the ionic liquids (IL201-203)

- *FT-IR*; Data recorded in table (3) and charts (1-3) illustrated the following:
  - The FT-IR spectra of compounds (IL<sub>201-203</sub>) show the presence of bands that indicate the stretching vibrations of benzene C-H bonds. These bands can be observed within the range of 3140-3043 cm<sup>-1</sup>. Additionally, the stretching vibrations of aromatic C=C are present in the spectra at the regions of 1492, 1504, and 1504 cm<sup>-1</sup> respectively.
  - The broad stretching bands of N-H that can be observed at 3417, 3441-3417, and 3417 cm<sup>-1</sup> in  $(IL_{201-203})$  are believed to be present due to the carbene proton in the form of NH<sup>+</sup> being present in the imidazole ring, according to reference [47].
  - $\circ~$  The stretching bands of aromatic C-H can be observed at 3136, 3140-3043, and 3140-3047 cm  $^{-1}$  respectively.
  - $\circ~$  The stretching bands of aliphatic C-H can be observed at 2904-2864, 2927-2854, and 2927-2854  $\rm cm^{-1}.$
  - $\circ$  All of the distinct imidazole region bands were obtained with precision [41].

	(v cm <sup>-1</sup> )												
									Imidazole zone				
IL	NH+	CH Ar	CH Aliphatic	C=C Ar	C-C Ar	C-C	C-N	C-H in plane bending	C-H out of plane bending	Ring deformation in plane bending	Ar bending zone	Ring deformation out of plane	
IL <sub>201</sub>	3417	3136	2904, 2864	1492	1465	1562	1415, 1364	1292, 1157	756	1087, 960	848, 756	628.79	
IL <sub>202</sub>	3441 - 3417	3140, 3043	2927, 2854	1504	1465	1562	1465, 1384	1315, 1249	756	1087, 921	810, 756	628.79	
IL <sub>203</sub>	3417	3140, 3047	2927, 2854	1504	1465	1562	1465, 1384	1323, 1157	752	1091, 925	810, 752	628.79	

Table 3: IR (v cm<sup>-1</sup>) of the ionic liquids (IL<sub>201-203</sub>).





•  ${}^{I}H$ -NMR; Data recorded in charts (4-6) can be interpreted as tabulated in table (4).

т		Proton type (δ ppm)												
IL	a	b	С	d	e	f	g	h	i	j	k	l	М	n
IL201	9.36	9.26 doublet	8.985	8.88 triplet	8.74 doublet	8.11 doublet	7.90 doublet	6.34	5.13	2.67	2.62	1.23	0.85	-
IL202	9.46	9.24 doublet	9.04	8.07 triplet	7.97 doublet	7.85 doublet	7.50 doublet	4.61	4.18	2.50	1.92	1.78	1.23	0.85
IL203	9.34	9.17 doublet	9.04	8.07 triplet	7.83 doublet	7.71 doublet	7.50 doublet	4.55	4.17	2.50	1.91	1.25	0.86	-

## Table 4: Chemical Shift (δ ppm) for ionic liquids (IL<sub>201-203</sub>).

In the above table, the  $\delta$  values of doublet and triplet protons are on average.



IL<sub>201</sub>



IL<sub>202</sub>



IL<sub>203</sub>

## Figure 1: type of protons for compounds IL<sub>201-203</sub>



**4.2 Surface activity:** Since the synthesized ionic liquids have the same hydrophilic groups (heads) and the same hydrophobic chains (tails) but differ in spacer chain lengths; the crucial factor that determines differences in surface properties should be the spacer chain lengths. Therefore, the surface activity was investigated for these asymmetric ionic liquids by measuring the critical micellar concentrations (CMC) determined from the conductance measurements, surface tension at the determined CMC ( $\gamma_{CMC}$ ), and PC<sub>20</sub>. The surface excess concentration ( $\Gamma_{max}$ ) and minimum area per molecule at the air–water interface (A<sub>min</sub>) determined from surface tension data using equations (i and ii) [48]–[50].

$$\Gamma_{max} = -1/nRT \left( d\gamma / dlnC \right) \tag{i}$$

$$A_{min} = 10^{16} / N_A \, \Gamma_{max} \tag{ii}$$

Where R is the universal gas constant, T is temperature,  $\gamma$  is the surface tension, and N<sub>A</sub> is Avogadro's number. The constant "n" either equal 2 for an ionic surfactant where the surfactant ion and the counter

ion are univalent or equal 3 for a dimeric surfactant made up of a divalent surfactant ion and two univalent counter ions, in the absence of a swamping electrolyte [49]. Hence a value of n = 3 was used in Eq. (i) for the present ionic dimeric surfactant system.

Compound	CMC mol./L	YcMc mN/m	π <sub>CMC</sub> mN/m	$PC_{20}$	Γ <sub>max</sub> X 10 <sup>11</sup> mol./ cm <sup>2</sup>	${ m A}_{ m min}$ ${ m nm}^2$	ΔG° <sub>mic</sub> KJ/mol	ΔG° <sub>ads</sub> KJ/mol
IL <sub>201</sub>	7 x10 <sup>-3</sup>	33	39	5.5x10 <sup>-5</sup>	10.276	1.616	-12.296	-50.248
IL <sub>202</sub>	8 x10 <sup>-3</sup>	35	37	1x10 <sup>-4</sup>	11.020	1.506	-11.964	-45.541
IL <sub>203</sub>	8 x10 <sup>-5</sup>	32	40	1x10 <sup>-5</sup>	11.644	1.426	-23.376	-57.729

Table 5: Surface parameters of the synthesized surfactants [IL<sub>201-203</sub>]

As shown in Table 5, The obtained CMC values are low. Thanks to strong hydrophobic interaction between multiple hydrocarbon chains, the ionic liquid compounds formed compact micelles. During surface activity investigation; it was observed that, the compound that has a long spacer chain, has the lowest  $\gamma_{CMC}$  value, thus has the best effectiveness of surface tension reduction also it has the lowest area occupied per molecule (A<sub>min</sub>) due to the spacer may penetrate into the hydrophobic core. So, with increasing spacer chain length, the surface-active molecules settled more closely at the air/water interface, thus A<sub>min</sub> decreased, while adsorption at the air-water interface ( $\Gamma_{max}$ ) conversely increased. This is due to the decrease in repulsion between the oriented ionic heads at the interface when the spacer bends more to the hydrophobic phase, adsorbing as a folded, wicket-like conformation [51].

The difference between the surface tension of IL<sub>201-203</sub> at their CMC and that of pure water is termed "effectiveness" ( $\pi_{CMC}$ ):  $\pi_{CMC} = \gamma_0 - \gamma$ 

where  $\gamma_0$  is the surface tension of the pure water and  $\gamma$  is the surface tension of the solution at CMC [52]. The effectiveness of the IL<sub>201-203</sub> ranged between 39 and 40 dyne/cm at 25°C (Table 5). The most efficient surfactant was the one that lowered the surface tension at the CMC. It is illustrated that these compounds are efficient in achieving the maximum reduction of the surface tension at CMC.

Efficiency (PC<sub>20</sub>): The PC<sub>20</sub> values were determined in Table (5). PC<sub>20</sub> is the bulk surfactant concentration needed to reduce the surface tension of the solvent by an arbitrary 20 mNm<sup>-1</sup>. This value commonly characterized the efficiency of a surfactant to lower surface tension. Values of C20 showed that IL<sub>201-203</sub> indicated that they have great efficiency in reducing the surface tension of water and consequently, have high surface activity.

Standard free energy of micellization ( $\Delta G^{\circ}_{mic}$ ), and standard free energy of adsorption ( $\Delta G^{\circ}_{ads}$ ):

 $\Delta G^{\circ}_{mic}$  is calculated as follows:

$$\Delta G^{o}_{mic} = RT \ln CMC$$

 $\Delta G^{\circ}_{mic}$  for the synthesized IL<sub>201-203</sub> surfactant were always negative values, indicating that micellization was a spontaneous process. The general trend of  $-\Delta G^{\circ}_{mic}$  increased with increasing the distance between the two heads groups (spacer), i.e., it became less negative. This indicates that increasing the spacer length and hydrophobicity favors the micellization process. Conversely,  $\Delta G^{\circ}_{ads}$  can be calculated by the relation

$$\Delta G^{o}_{ads} = \Delta G^{o}_{mic} - (0.6x \,\pi_{cmc} x A_{min})$$

Table 5 shows some increase in  $\Delta G^{\circ}_{ads}$ , supporting the idea of micellization over adsorption on the solution surface to overcome the repulsion forces occurring at the water/hydrophobe interface.  $\Delta G^{\circ}_{ads}$  and  $\Delta G^{\circ}_{mic}$  were always negative in value due to the spontaneity, and indicating that the processes are thermodynamically favored [53], [54].



Figure 2: Surface tension isotherms of IL<sub>201-203</sub> at 25 °C

**4.3 Effect of IL**<sub>201-203</sub> as base oil improvers: The impact of these compounds as base oil improvers was tested via:

Enhancement of Total Acid Number values (TAN): The total acid number serves as a helpful tool for quality control of lubricating oil, as well as a way to determine lubricant degradation during use [55]. Figure 3 depicts the changes the total acid number of the blank sample during oxidation (over a period of 96 hours at 120 °C, from zero time). As time progresses, TAN clearly increases due to the oil chains oxidizing to form acidic species and subsequently leading to a rise in the oil's acid content (Scheme 1).







Scheme 1: Oxidation of the base stock oil

In the presence of additives (IL<sub>201-203</sub>), the thermal oxidation of the tested base oil is reduced at the same conditions, (a period of 96 hrs. at 120 °C). This is due to the effect of the presence of additives, which in turn prolong the oxidation period, or more precisely, reduce the oxidation of the tested base oil. Table 6 and figures (4-6) demonstrate the total acid number values before and after the presence of additives. With increasing concentrations of additives, ranging from 200, 400 and 600 ppm, the TAN

values noticeably decrease, (from 0. 3658 to 0.2771 mg KOH/g, 0.3016 to 0.1111 mg KOH/g, and 0.1453 to 0. 0661 mg KOH/g respectively. This indicates that the stability of the base oil is increased by mixing the prepared compounds, where IL<sub>203</sub> is the most efficient, followed by IL<sub>202</sub> and IL<sub>201</sub>.

Sampla	m) s	Time intervals (hrs.)						
Sample	(pp Co II	24	48	72	96			
Base oil Blank (without additive)	0	0.2621	0.4636	0.7056	0.9130			
IL201	200	0.1812	0.2874	0.3159	0.3658			
	400	0.0715	0.1779	0.2235	0.3016			
	600	0.0441	0.0555	0.0789	0.1453			
П 202	200	0.1785	0.1985	0.2652	0.2885			
11202	400	0.0558	0.101	0.2015	0.2435			
	600	0.0412	0.0494	0.0752	0.0857			
IL 203	200	0.0545	0.0998	0.1356	0.2771			
	400	0.0321	0.0366	0.0665	0.1111			
	600	0.0285	0.0309	0.049	0.0661			

Table 6: Variation of total acid number (mg KOH/g) without and with IL<sub>201-203</sub>



Figures 4, 5 and 6: TAN (mg KOH/g) variation of the base oil with and without IL<sub>201</sub>, IL<sub>202</sub>, and IL<sub>203</sub> (respectively) of concentrations 200, 400, and 600 ppm

Viscosity: The studied base oil sample showed an increase in viscosity and the buildup of varnish and sludge due to oxidation, as shown in Table 7. The blank sample had a high viscosity reading (15.70 mm<sup>2</sup>/s) after being oxidized for 96 hrs. However, after adding the prepared compounds with varying concentrations, as shown in Table 7 and Figures 7-9, the viscosity values improved significantly. These results indicated that the prepared additives have a positive effect on the oxidation stability of the base oil sample.

Sample	n) s	Time Intervals (hrs.)					
	Cor Cor	24	48	72	96		
Base oil	0	15.60	15.62	15.66	15.70		
	200	15.45	15.47	15.53	15.59		
IL <sub>201</sub>	400	15.41	15.45	15.48	15.50		
	600	15.40	15.41	15.46	15.48		
	200	15.46	15.48	15.55	15.59		
IL <sub>202</sub>	400	15.43	15.46	15.50	15.53		
	600	15.41	15.43	15.48	15.50		
	200	15.49	15.52	15.55	15.58		
IL <sub>203</sub>	400	15.45	15.49	15.51	15.54		
	600	15.44	15.46	15.49	15.51		

Table 7: Variation of viscosity at 100°C (mm2/s) with and without IL<sub>201-203</sub>



Figures 7, 8 and 9: Viscosity (mm<sup>2</sup>/s) variation of the base oil with and without IL<sub>201</sub>, IL<sub>202</sub>, and IL<sub>203</sub> (respectively) of concentration: 200, 400, and 600 ppm

• Effect of  $IL_{201-203}$  on foaming characteristics: Oil-lubricated components often face the challenge of foaming. Foam is the accumulation of tiny air bubbles on or around the fluid's surface, which can lead to various issues such as increased oxidation, pump cavitation, micro dieseling [56], loss of oil's lubricating properties, and ultimately hydraulic system failure. The ASTM D892-18 foaming characteristics test is used to evaluate these concerns. According to Table 8, it has been demonstrated that the blank sample has unsatisfactory foaming characteristics. This can be attributed to the high foaming volume of 170 ml, which collapses after a prolonged period of 480 seconds. Table 8 and figures 10a-12b indicated that the addition of different concentrations of prepared additives to the base oil has resulted in improved foaming characteristics. In comparison to the blank sample, the foaming volume has reduced from 170 ml to 67 ml, whereas the foaming collapse time has improved from 480.03 to 122.09 seconds. The antifoaming efficiency of the additives has been ranked as  $IL_{203} > IL_{202}$ 

Sample	ILs Conc. (ppm)	Foaming Volume(ml)	Foaming Collapse Time (s)
Base oil	0	170	480.03
(Blank without additive)			
IL 201	200	118	214.35
11201	400	112	207.01
	600	97	179.39
IL 202	200	101	187.25
11202	400	92	171.89
	600	78	149.52
IL.203	200	97	180.13
	400	78	146.35
	600	67	122.09



Table 8: Variation of foaming volume (ml) at 50 °C with and without additives

Figures 10, 11, and 12(a): Foaming volume (ml) variation of the base oil with and without  $IL_{201}$ ,  $IL_{202}$ , and  $IL_{203}$  (respectively) of concentrations 200, 400, and 600 ppm



Figures 10, 11, and 12 (b): Foaming collapse time (s) variation of the base oil with and without IL<sub>201</sub>, IL<sub>202</sub>, and IL<sub>203</sub> (respectively) of concentrations 200, 400, and 600 ppm

## 5. CONCLUSION

- The physicochemical characteristics of the delivered hydro-finished base oil are described according to ASTM.
- The structures of the three synthesized compounds (IL<sub>201-203</sub>) were well identified and elucidated.
- Their surface parameters indicated that, they have good surface activity.
- They were tested as antioxidants and antifoams for local base oil, and their efficiency of them is ranked as follows: IL<sub>203</sub> > IL<sub>202</sub> >IL<sub>201</sub>.

Conflict of interest: There is no conflict of interest.

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## الملخص العربي

في هذا العمل، ثلاثة سوائل أيونية غير متماثلة، وهي:

1-(2-(1-decyl-1*H*-imidazolium-3-yl) ethyl)-3-methylpyridinium bromide (IL<sub>201</sub>),

1-(5-(1-decyl-1*H*-imidazolium-3-yl) pentyl)-3-methylpyridinium bromide (IL<sub>202</sub>), and

1-(10-(1-decyl-1*H*-imidazolium-3-yl) decyl)-3-methyl-pyridinium bromide (IL<sub>203</sub>)

تم تأكيد تركيبها الكيميائي من خلال التحليل الأولي للعناصر والتحليل الطيفي للأشعة تحت الحمراء والرنين المغناطيسي النووي الهيدروجيني. تم فحص الخواص السطحية لهذه السوائل الأيونية، التوتر السطحي، التركيز الحرج للمذيلة، الفعالية، الحد الأقصى للزيادة السطحية، والحد الأدنى من مساحة السطح، بتركيز ات مختلفة عند ٢٥ درجة مئوية. تم الحصول على الطاقات الحرة القياسية من micellization والامتزاز. تم در استها واختبار ها على أنها محسنات زيت قاعدي، وخاصة تبا الأكسدة، (من خلال در اسة التغير في العدد الكلي للحمض [TAN] واللزوجة)، وخصائص الرغوة. يتم تصنيف كفاءة هذه المركبات كمحسنات للزيوت الأساسية على النحو التالي، الدي10 الدي20 اله.