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## Asymmetric Dicationic Ionic Liquids: synthesis and evaluation as additive improvers for Egyptian Base Oil III

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#### ABSTRACT

In this work, we synthesized three distinct types of asymmetrical dicationic ionic liquids: 1-(2-(1-decyl-1H-imidazolium-3-yl)) ethyl) pyridinium bromide (IL<sub>301</sub>), 1-(5-(1-decyl-1H-imidazolium-3-yl)) pentyl) pyridinium bromide (IL<sub>302</sub>), and 1-(10-(1-decyl-1H-imidazolium-3-yl)) decyl) pyridinium bromide (IL<sub>303</sub>). Their structures were characterized by using the conventional techniques of analysis, (elemental analysis, Fourier Transform infrared spectroscopy and proton nuclear magnetic resonance). The surface characteristics of the synthesized asymmetrical dicationic ionic liquids, (surface tension, critical micelle concentration, effectiveness, maximum surface excess, and minimum surface area) were studied. Additionally, the standard free energies of micellization and adsorption were calculated for each compound. The efficiency of IL<sub>301</sub>, IL<sub>302</sub>, and IL<sub>303</sub> to enhance base oil was examined and recorded, specifically in terms of oxidation stability (measured through changes in total acid number [TAN] and viscosity) and foam characteristics. The data indicated that IL<sub>303</sub> was the most effective base oil enhancer, followed by IL<sub>302</sub> and IL<sub>301</sub>.

#### **Key Words:**

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

## 1. INTRODUCTION

Tribology, a field of study related to friction and wear of surfaces in motion, plays a crucial role in the operation, efficiency, and reliability of machines and devices that are important to countries' modern economy [1]. Tribology is essential in industry, where it is used to increase the efficiency of wind turbines, solar panels, and other renewable energy technologies. Tribology also has a significant impact on the environment, as reducing friction and wear can lead to reduced energy consumption and lower greenhouse gas emissions. This makes tribology an important consideration in sustainability and eco-efficiency efforts [2]–[5]. Consequentially, tribology is essential to the manufacturing industry. The dissipation of energy due to friction constitutes approximately 33% of global industrial energy usage,

while approximately 80% of part failures can be attributed to the deleterious effects of wear and tear [6]. So, we can extend the operational lifetime of the operating machinery by reducing friction and wear [7] which ultimately leads to improved productivity and reduced costs. Tribology has a significant impact on the transportation industry, where it is used to optimize fuel efficiency and reduce wear and tear on vehicles, ships, and aircraft [8]. Also, tribology is used in the medical applications to improve the performance of implants [9], prosthetics, and other medical devices. This helps to improve patient outcomes, reduce healthcare costs, and improve overall quality of life [10].

As countries tendency towards a more sustainable future, one of the key global goals is to promote prospective practices. By incorporating wear protection in machines, their service life and functionality should be extended, which requires fewer replacement machines for production and handling operations [11]. This in turn reduces the need for materials, primary energy, and work required for production, ultimately leading to lower emissions. In a revolving economy, [4], [12], [13], this concerned approach enables a more intensive use of materials in consumer products so improving wear protection and utilizing tribotronics and condition monitoring to increase service life are equally important to friction reduction in diminishing  $CO_2$  emissions and promoting energy efficiency through enhanced material efficiency and resource preservation. Industry and science have differing perspectives on sustainability and continuously evolving definitions. The German government's sustainability plan from 2017 is closely aligned with the United Nations' 17 sustainable development goals (SDGs) introduced in 2015, which are essential for promoting global sustainability. Tribology is known to positively impact at least six of these 17 SDGs [14]. The management of friction and wear is a widely acknowledged challenge that affects diverse material applications, including but not limited to gears and engine parts, medical implants designed for joint replacement, and micro- and nano-scale machine technologies [15].

Currently, the reduction of energy loss and material consumption resulting from friction and wear is primarily achieved through surface engineering, lubrication, wear-resistant materials, and tribological design. Among these, surface engineering and lubrication are the primary approaches for enhancing the tribological performance of materials. Lubrication, a technique that employs lubricants to decrease friction and wear between contact surfaces, is a significant technology in tribology [16]. Additionally, there has been notable advancement in comprehending the mechanism of friction and wear, as well as in the development of novel lubricating materials. These advancements have led to substantial reductions in friction and wear and improvements in lubrication protection. Employing lubrication in machinery and industrial settings is an efficacious strategy for managing friction and wear. Furthermore, with the innovation and integration of new lubricant additives, the potential of lubricants to mitigate friction and wear can be further augmented [6].

Lubrication is defined as the process of applying a substance (lubricant) between two sliding or rolling surfaces. They typically consist of a base oil, which can be mineral, synthetic or vegetable-based, and a range of additives that enhance their performance characteristics [17]. Whereas the lubricants are essential for achieving the tribological goal; the additives are crucial to enhance the functions of lubricants and extend their lifespan. These additives can include friction modifiers to improve efficiency and reduce wear, anti-wear (AW) additives that form a protective film on metal surfaces, antioxidants to prevent oxidation and degradation of the oil, detergents to clean surfaces, and viscosity improvers to maintain the oil's consistency at different temperatures. Additionally, lubricants may contain extreme pressure (EP) additives that allow them to withstand high pressures and temperatures. To guarantee optimal performance and avoid any negative consequences, it's crucial to verify that the additives used are compatible with both the base oil and with one another [18].

Ionic liquids, are a type of organic molten salts composed exclusively of cations and anions. Thanks to their exceptional physicochemical properties, such as low vapor pressure, high thermal stability, high surface tension, high shear viscosities, excellent thermal conductivity, wide electrochemical window, and low melting point, among others, Ionic liquids have a wide range of applications [19]. Recently, ionic liquids have gained attention as a promising alternative to traditional additives due to their impressive tribological characteristics, ash-free composition, lower emissions of hazardous materials, and overall eco-friendliness [13], [20]. Ionic liquids, when added to lubricant base oils, not only improve their tribological performance but also enhance their physiochemical properties while reducing their undesirable properties [21]–[24]. Ionic liquids have a strong ability to bind with metal surfaces, providing effective protection against wear and safeguarding the interacting surfaces from carbon deposits and soot [25]. The production of ionic liquids is expensive, which limits their use as standalone lubricants. However, they can be added as an additive to base oils to enhance their innate tribological properties, leading to improved lubrication performance [26], [27]. Ionic liquids have been studied as lubricant additives in the past. Based on the published research, it can be concluded that ionic liquids are highly effective at forming a strong anti-wear film, minimizing corrosion, and enduring heavy loads [28]–[32].

### 2. STUDY AREA

In our prior research, we developed and investigated various heterocyclic compounds [33]–[39], azophenols [40], and azo-liquid crystals [41]–[43] for improving base oils. These compounds were used as antioxidants, viscosity improvers, and pour point depressants. Also; a series of dicationic ionic liquids were synthesized [19] and their performance as base oil improvers was evaluated. The current work (III) of this series involves the synthesis and testing of a set of asymmetric dicationic ionic liquids for their ability to improve the oxidation stability, viscosity, and foaming prevention properties of the base oil.

### 3. MATERIALS AND METHODS

**3.1 Samples collection and analysis:** For this study, a liquid paraffin-based oil provided by Co-operation Petroleum Company was utilized. The physical and chemical characteristics of the oil were measured in accordance with the standards set by the American Society of Testing Materials (ASTM), as outlined in 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 @ 100 °C	165.33 15.56	ASTM D445
Viscosity Index (VI)	95	ASTM D2270
Total Acid Number (TAN)	0.061	ASTM D664
Foaming Characteristics at 50°C, Foaming Volume (ml) Collapse Time (s)	170 480	ASTM D892
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	

**3.2 Synthesis of dicationic ionic liquids IL**<sub>301-303</sub>**:** The chemicals and solvents utilized in this study were obtained from reputable international chemical companies and were used without any additional purification. Specifically, the materials employed included anhydrous acetonitrile, 99.5% ethyl acetate, absolute ethyl alcohol, 98% 1-bromodecane, 99% 1*H*-imidazole, 98% petroleum ether (40-60), and 97% potassium hydroxide from Merck Co. Additionally, 99% pyridine, 99% 1,2-dibromoethane, 99% 1,5-dibromopentane, and 99% 1,10-dibromodecane from Alfa Aesar Co. were also used.

### Steps of synthesis were illustrated as follows:

I-decy-1*H*-imidazole was prepared previously [19], [44]. In a conical flask, 1*H*-imidazole (0.1 mol) and potassium hydroxide (0.1 mol) were dissolved in 50 ml acetonitrile with stirring at room temperature. 1-Bromodecane (0.11 mol) was added dropwise for one hour. Stirring is continued till 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-1H-imidazole

Compounds 301, 302 and 303 were synthesized by mixing pyridine (0.01 mol) with dibromo alkanes (1,2-dibromoethane, 1,5-dibromopentane, and 1,10-dibromodecane) (0.015 mol) and stirred the mixture for 24 hours at room temperature. The mixture is then washed with ethyl acetate several times to remove any unreacted compounds. After that, the products are purified using petroleum ether 40-60. Finally, they were collected under vacuum, Equation 2 [45].





301; n = 2, 1-(2-bromoethyl)-pyridin-1-ium bromide

302; n = 5, 1-(5-bromopentyl)-pyridin-1-ium bromide

303; n =10, 1-(10-bromodecyl)-pyridin-1-ium bromide

Synthesis of Ionic Liquids IL<sub>301-303</sub>: In order to prepare These compounds, 1-decyl-1*H*-imidazole, (0.01 mol), was refluxed with compounds 301-303 (0.01 mol) in 50 ml acetonitrile for 12 hours at 80°C. After that, the products are purified via evaporation of acetonitrile under vacuum, Equation 3 [46].



Eq 3: Preparation of IL<sub>301-303</sub>

IL<sub>301</sub>: n = 2, 1-(2-(1-decyl-1*H*-imidazol-3-ium-3-yl) ethyl)-pyridin-1-ium bromide.

IL<sub>302</sub>: n = 5, 1-(5-(1-decyl-1*H*-imidazol-3-ium-3-yl) pentyl)-pyridin-1-ium bromide.

IL<sub>303</sub>: n = 10, 1-(10-(1-decyl-1*H*-imidazol-3-ium-3-yl) decyl)-pyridin-1-ium bromide.

We used different tools of analysis, (Elemental Analysis (Elementary Viro El Micro-analysis), 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). For the <sup>1</sup>H-NMR spectra, we used DMSO as the solvent. These tools allowed us to thoroughly characterize the synthesized compounds.

**3.3 Surface tension measurements:** Du Noüy tensiometer are used with a platinum ring to conduct surface tension measurements. we prepared fresh aqueous solutions of asymmetric IL<sub>301-303</sub> dicationic ionic liquids and determined their surface tension over a concentration range of 0.01-0.000001 M/L at a temperature of 25°C. Prior to taking measurements, we calibrated the instrument using the surface tension value of double-distilled water, which is typically 72.00  $\pm$  0.50 mN/m. For each sample solution, we prepared it with double-distilled water and let it stabilize for 5 minutes in the instrument before taking measurements. To minimize error, we repeated each measurement three times [47], [48].

**3.4 Total Acid Number (TAN):** We used ASTM D664 [49] and a Metrohm Titrando 905 potentiometer, stirrer 801, and electrode model 6.0229.010 to determine the total acid number of the base oil before and after adding the three  $IL_{301-303}$ . We followed the instrument parameters outlined in Metrohm Application Bulletin AB-404/2e..

**3.5 Viscosity:** We measured the kinematic viscosity of the base oil before and after adding the three IL<sub>301-303</sub> using CT-1000 CANON oil bath, Cannon-Fenske viscometers size 150, and Kohler thermometer instrument. To do this, we followed ASTM D445 [50].

**3.6 Foaming characteristics:** ASTM D892 [51] is used for determination of Foaming characteristics for base oil before and after  $IL_{301-303}$  addition using Petrotest DP water bath and ZEAL DM3A gas meter.

# 4. RESULTS AND DISCUSSION

# Physico-chemical parameters

# 4.1 Characterization of IL<sub>301-303</sub>:

• *Elemental analysis*; The obtained results of the elemental analysis described in Table 2 closely agree with the calculated data.

IL	С%		Н%		N%		Br%		Mol. Wt.	Yield %
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.		
IL <sub>301</sub>	50.54	50.49	7.00	7.11	8.84	8.72	33.62	33.67	475	78
IL <sub>302</sub>	53.39	53.20	7.60	7.65	8.12	8.07	30.89	31.06	517	75
IL <sub>303</sub>	57.24	57.26	8.41	8.33	7.15	7.11	27.20	27.29	587	80

# Table 2: Elemental analysis of the ionic liquids (IL<sub>301-303</sub>)

- *FT-IR*; Data recorded in table (3) and charts (1-3) illustrated the following:
  - In the FT-IR spectra of compounds (IL<sub>301-303</sub>), the aromatic stretching vibrations bands of benzene C-H bonds are observed in the range of 3132-3056 cm<sup>-1</sup>. Stretching vibrations bands of aromatic C=C are observed in the regions of 1574, 1565-1512 and 1584 cm<sup>-1</sup> respectively.
  - N-H broad stretching bands, appeared at 3423, 3424 and 3424 cm<sup>-1</sup>, for (IL<sub>301-303</sub>) are attributed to the presence of the carbene proton in the form of NH<sup>+</sup> in imidazole ring [35].
  - The Aromatic C-H stretching bands appeared at 3129-3056, 3131-3090, and 3132-3058 cm<sup>-1</sup> respectively.
  - Aliphatic C-H (stretching) bands appeared at 2926-2856, 2925-2856 and 2926-2856 cm<sup>-1</sup>.
  - All the specific imidazole zone bands were obtained precisely [46].

	(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 hending	Ar bending zone	Ring deformation out of plane		
IL <sub>301</sub>	3423 broad	3129 - 3056	2926 , 2856	1574	1483	1630	1375	1200, 1171	775	1088, 950	775, 678	628.65		
IL <sub>302</sub>	3424 broad	3131 - 3090	2925 , 2856	1565 , 1512	1463	1641	1406 1374	1232, 1166	730	1061, 913	829, 730	626		
IL <sub>303</sub>	3424 broad	3132 , 3058	2926 , 2856	1584	1460	1632	1370	1224, 1166	771	1082	728, 681	629		



Table 3: IR (v cm<sup>-1</sup>) of the ionic liquids (IL<sub>301-303</sub>).

Chart 1: IR spectrum of IL<sub>301</sub>



Chart 2: IR spectrum of IL<sub>302</sub>



Chart 3: IR spectrum of IL<sub>303</sub>

•  ${}^{1}H$ -NMR; Data recorded in charts (4-6) can be interpreted as tabulated in table (4).

	Proton	Proton type (δ ppm)										
IL	a	b	c	d	e	f	g	h	i	j	k	1
IL <sub>301</sub>	9.31	9.21	8.71	8.24	7.86	7.71	6.42	5.88	4.20	1.78	1.21	0.83
IL <sub>302</sub>	9.39	9.05	8.00	7.85	7.26	7.21	4.61	4.20	2.56	1.96	1.22	0.86
IL <sub>303</sub>	9.435	9.04	8.05	7.98	7.85	7.23	4.20	3.99	2.62	1.70	1.206	0.85

Table 4: Chemical Shift (δ ppm) for ionic liquids (IL<sub>301-303</sub>).







Figure 1: type of protons for compounds IL<sub>301-303</sub>



Chart 6: NMR spectrum of IL<sub>303</sub>

**4.2 Surface activity:** Despite the synthesized ionic liquids consist of identical hydrophilic groups (heads) and hydrophobic chains (tails), the variation in spacer chain lengths is presumed to be the key factor that determines the differences in surface properties. As a result, we delved into the investigation of surface activity for this type of ionic liquids using critical micellar concentrations (CMC) obtained from conductance measurements, surface tension at the determined CMC ( $\gamma_{CMC}$ ), and PC<sub>20</sub>. Equations (i and ii) determined the surface excess concentration ( $\Gamma_{max}$ ) and the minimum area per molecule at the air-water interface (A<sub>min</sub>) from surface tension data [52]–[54].

$$\Gamma_{\text{max}} = -1/\text{nRT} (d\gamma / d\text{lnC})$$
(i)  
$$A_{\text{min}} = 10^{16} / \text{NA} \Gamma_{\text{max}}$$
(ii)

Where R is the universal gas constant, T is the temperature,  $\gamma$  surface tension, and Avogadro's number (NA). For compounds IL<sub>301-303</sub>, (dimeric surfactant composed of a divalent surfactant ion and two univalent counterions) the constant "n" equals 3 [53].

Compound	CMC mol/L	үсмс <b>т</b> N/ <b>т</b>	π <sub>CMC</sub> mN/m	$PC_{20}$	Γ <sub>max</sub> X 10 <sup>11</sup> mol./ cm <sup>2</sup>	${f A}_{ m min}$ ${ m nm}^2$	ΔG° <sub>mic</sub> KJ/mol	ΔG° <sub>ads</sub> KJ/mol
IL <sub>301</sub>	5.5 x10 <sup>-5</sup>	34	38	4.5x10 <sup>-6</sup>	9.74	1.705	-24.305	-63.328
IL <sub>302</sub>	1 x10 <sup>-4</sup>	33	39	8x10 <sup>-6</sup>	9.74	1.705	-22.823	-62.873
IL <sub>303</sub>	4 x10 <sup>-4</sup>	33	39	1.8x10 <sup>-5</sup>	7.76	2.139	-19.388	-69.633

Table 5: Surface parameters of the synthesized surfactants [IL<sub>301-303</sub>]

Table 5 displays low CMC values that can be attributed to the robust hydrophobic interactions among the multiple hydrocarbon chains, which lead to the formation of compact micelles in the ionic liquid compounds. Upon investigating their surface activity, we noticed that the compound with a long spacer chain exhibited the lowest  $\gamma_{CMC}$  value, indicating the most effective reduction in surface tension. Additionally, this compound had the lowest area occupied per molecule (A<sub>min</sub>) due to the possibility of the spacer penetrating the hydrophobic core. So, an increase in spacer chain length resulted in the surfaceactive molecules settling more closely at the air-water interface, leading to a decrease in Amin. Conversely, adsorption at the air-water interface ( $\Gamma_{max}$ ) increased. This phenomenon occurred because the repulsion between the oriented ionic heads at the interface decreased when the spacer bent more towards the hydrophobic phase, leading to adsorption in a folded, wicket-like conformation [55].

The term effectiveness, ( $\pi_{CMC}$  Equation iii), refers to the difference between the surface tension of IL<sub>301-303</sub> at their CMC, ( $\gamma$ ), and that of pure water, ( $\gamma_0$ ), [56].

$$\pi_{\rm CMC} = \gamma_0 - \gamma \tag{iii}$$

Table 5 shows that the effectiveness of  $IL_{301-303}$  ranged between 39 and 40 dyne/cm at 25°C. The most efficient surface-active compound was the one that lowered the surface tension at the CMC.

The efficiency of these compounds in lowering surface tension,  $PC_{20}$  values, was determined in Table (5).  $PC_{20}$  refers to the bulk surfactant concentration required to decrease the surface tension of the solvent by 20 mNm-1. It is obviously recorded that ionic liquids  $IL_{301-303}$  showed exceptional surface activity and efficiency in reducing surface tension of water, as reflected by their high  $PC_{20}$  values.

The calculation of standard free energy of micellization ( $\Delta G^{\circ}_{mic}$ ), and standard free energy of adsorption ( $\Delta G^{\circ}_{ads}$ ) according to the equation (iv):

$$\Delta G^{\circ}_{mic} = RT \ln CMC \qquad (iv)$$

The synthetic compounds  $IL_{301-303}$  exhibited consistently negative values for  $\Delta G^{\circ}_{mic}$  which is consistent with spontaneous micellization. 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 indicated that increasing in the spacer length and hydrophobicity favor the micellization process.

On the other hand,  $\Delta G^{\circ}_{ads}$  can be determined using the following equation

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

Table 5 showed a slight increase in  $\Delta G^{\circ}_{ads}$  which is consistent with the theory that micellization is more likely than adsorption on the solution surface because it overcomes the repulsion forces at the water/hydrophobe interface. Both  $\Delta G^{\circ}_{ads}$  and  $\Delta G^{\circ}_{mic}$  were negative, indicating that these processes occur spontaneously and are thermodynamically favored [57], [58].



Figure 2: Surface tension isotherms of IL<sub>301-303</sub> at 25 °C

**4.3 Base oil improvement:** The recorded study showed a significant effect of the prepared compounds as improving the physicochemical characteristics of the tested base oil through the following:

Change in Total Acid Number values (TAN): The total acid number is a point of reference for lubricating oil quality control. It is additionally used as a measure of lubricant deterioration in service [59]. Figure 3 illustrated how the blank sample affected by oxidation process, (from zero time up to 96 h, at 120 °C). It is evident that as time increased the rate of oxidation is increased. This is attributed to the possibility that the base oil is contaminated with acidic constituents during the oxidation process which lead to increase in acid content of the oil sample, Scheme 1.



Figure 3: Variation of TAN values of blank sample with time



Scheme 1: Oxidation of the base stock oil

After 96 hours of thermal oxidation testing, the maximum TAN values were observed (Table 6). Upon adding the  $IL_{301-303}$  compounds at various concentrations, the total acid number values decreased. Table 6 and figures (4-6) demonstrated that the TAN values decreased with increasing concentrations of the  $IL_{301-303}$  compounds, ranging from 200 up to 600 ppm, during the thermal oxidation of the base oil up to 96 hours. As an example, when adding  $IL_{301}$ , values ranging from 0.1706 to 0.3215 mg KOH/g (200 ppm), 0.0658 to 0.2556 mg KOH/g (400 ppm), and 0.0411 to 0.1254 mg KOH/g (600 ppm) were recorded. Figures (4-6) also revealed that the stability of the base oil was enhanced upon adding the  $IL_{301-303}$  compounds, in the order:  $IL_{302} > IL_{302} > IL_{301}$ .

Sample	s. nc.		m)	Time intervals (hrs.)					
	Π	Co	dd)	24	48	72	96		
Base oil	0			0.2621	0.4636	0.7056	0.9130		
	200			0.1706	0.1998	0.2705	0.3215		
IL <sub>301</sub>	400			0.0658	0.1280	0.1916	0.2556		
	600			0.0411	0.0501	0.0668	0.1254		
ч	200			0.1601	0.1775	0.1998	0.2215		
$IL_{302}$	400			0.0581	0.0756	0.0912	0.1232		
	600			0.0401	0.0444	0.0512	0.0661		
п	200			0.0476	0.0914	0.1123	0.2095		
$1L_{303}$	400			0.0309	0.0323	0.0506	0.0889		
	600			0.0296	0.0315	0.0389	0.0505		

Table 6: Variation of total acid number (mg KOH/g) without and with IL<sub>301-303</sub>



Figures 4, 5 and 6: TAN (mg KOH/g) variation of the base oil with and without IL<sub>301</sub>, IL<sub>302</sub>, and IL<sub>303</sub> (respectively) of concentrations 200, 400, and 600 ppm

Viscosity: As well known, sludge poses numerous risks to engine performance. Firstly, it restricts the flow of oil, hindering its ability to lubricate engine components effectively. This can result in increased friction, accelerated wear and tear, and reduced fuel efficiency [8]. Oxidation of the tested base oil sample lead to an increase in the oil's deposits, (varnish and sludge-a thick gelatinous substance that accumulates within the engine), which is accompanied with an increase in its viscosity (Table 7). The blank sample gave high reading (15.70 mm<sup>2</sup>/s) in viscosity value after heating at 120 °C for 96 hours. The viscosity values showed good results after adding the prepared compounds with different concentrations, table 7 and figures (7-9). These results illustrated that; the oxidation stability is improved, (i.e., sludge residue is reduced and consequently viscosity is decreased), in presence of the prepared additives.

Sample	• ~	Time Intervals (hrs.)						
Sumple	ILs Conc (ppm	24	48	72	96			
Base oil	0	15.60	15.62	15.66	15.70			
Blank (without additive)								
	200	15.42	15.44	15.48	15.51			
IL <sub>301</sub>	400	15.40	15.41	15.44	15.48			
	600	15.37	15.39	15.40	15.44			
	200	15.44	15.46	15.50	15.53			
IL <sub>302</sub>	400	15.42	15.43	15.47	15.50			
	600	15.39	15.42	15.44	15.48			
~~	200	15.47	15.49	15.51	15.54			
$IL_{303}$	400	15.44	15.47	15.50	15.53			
	600	15.41	15.44	15.47	15.50			

Table 7: Variation of viscosity at 100°C (mm<sup>2</sup>/s) with and without IL<sub>301-303</sub>



Figures 7, 8 and 9: Viscosity (mm<sup>2</sup>/s) variation of the base oil with and without IL<sub>301</sub>, IL<sub>302</sub>, and IL<sub>303</sub> (respectively) of concentration: 200, 400, and 600 ppm

• Foaming characteristics: One of the important physical properties of lubricants is the resistance of lubricant to the creation of foam. Foaming is a common problem with oil-lubricated components [60]. The foam acts as an insulator and reduces a lubricant's cooling abilities, resulting in overheating. Foam can also lead to poor performance, mechanical failure, costly repairs, and a shortened operability lifetime due to an inability to lubricate effectively or undergo cavitation. With foaming characteristics test, (ASTM D892), the blank sample was proven bad foaming characteristics where the obtained foaming volume is considered high (170 ml) with long time (480 s) for foaming collapse (Table 8). By adding anti-foaming agents, (IL<sub>301-303</sub> quarterly ammonium salts), the creation of stable foam in oil is prevented. Antifoaming agents act in such a way that they decrease the surface tension of air bubbles, breaking them into smaller bubbles, or destroying them on the surface, thus contributing to quick decomposition of foam [61]. As shown in Table 8 and figures 10a-12b, the foaming volumes were reduced compared to the blank sample, (from 170 decreased to 65 ml). Also, the foaming collapse time was reduced from 480.03 to 137.3 s. The efficiency of the additives as antifoams is ranked as follows: IL<sub>303</sub> > IL<sub>302</sub> > IL<sub>301</sub>.

Sample	ILs Conc. (ppm)	Foaming Volume(ml)	Foaming Collapse Time (s)
Base oil	0	170	480.03
(Blank without additive)			
n	200	122	229.83
1L <sub>301</sub>	400	114	210.03
	600	99	181.23
п	200	109	202.76
IL <sub>302</sub>	400	95	175.43
	600	82	151.36
п	200	100	185.36
112303	400	85	157.96
	600	72	137.3

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<sub>301</sub>, IL<sub>302</sub>, and IL<sub>303</sub> (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>301</sub>, IL<sub>302</sub>, and IL<sub>303</sub> (respectively) of concentrations 200, 400, and 600 ppm

### 5. CONCLUSION

- The delivered base oil sample was characterized via the ASTM methods of analysis.
- The three compounds (IL<sub>301-303</sub>) were prepared and their chemical structures were well elucidated using the different tools of analysis.
- Their surface parameters indicated that, they have good surface activity.
- They were tested as antioxidants and antifoams for the tested base oil, and the efficiency of them is ranked as follows: IL<sub>303</sub> > IL<sub>302</sub> >IL<sub>301</sub>.

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#### 6. **REFERENCES**

- [1] P. Lan, J. L. Meyer, B. Vaezian, and A. A. Polycarpou, "Advanced polymeric coatings for tilting pad bearings with application in the oil and gas industry," *Wear*, vol. 354–355, pp. 10–20, 2016, doi: https://doi.org/10.1016/j.wear.2016.02.013.
- [2] I. Tzanakis, M. Hadfield, B. Thomas, S. M. Noya, I. Henshaw, and S. Austen, "Future perspectives on sustainable tribology," *Renew. Sustain. Energy Rev.*, vol. 16, pp. 4126–4140, 2012, doi: 10.1016/j.rser.2012.02.064.
- [3] N. Van Minh, A. Kuzharov, L. H. Ninh, N. Huynh, and A. Kuzharov, "Green Tribology," in *Tribology in Materials and Manufacturing*, A. Patnaik, T. Singh, and V. Kukshal, Eds. Rijeka: IntechOpen, 2020.
- [4] D. G. Eskin, M. Hadfield, B. D. H. Thomas, S. M. Noya, I. Henshaw, and S. Austen, "Future perspectives on sustainable tribology," *Renew. Sustain. Energy Rev.*, vol. 16, no. 6, pp. 4126–4140, 2012, doi: 10.1016/j.rser.2012.02.064.
- [5] M. Woydt, "The importance of tribology for reducing CO2 emissions and for sustainability," *Wear*, vol. 474–475, p. 203768, 2021, doi: https://doi.org/10.1016/j.wear.2021.203768.
- [6] J. Sun and S. Du, "Application of graphene derivatives and their nanocomposites in tribology and lubrication: a review," *RSC Adv.*, vol. 9, no. 69, pp. 40642–40661, 2019, doi: 10.1039/c9ra05679c.
- [7] G. Cañellas *et al.*, "Tribological Performance of Esters, Friction Modifier and Antiwear Additives for Electric Vehicle Applications," *Lubricants*, vol. 11, no. 3, 2023, doi: 10.3390/lubricants11030109.
- [8] N. K. Myshkin and F. A. Grigoriev, "Green Tribology for Sustainable Development Goals," in Proceedings of I4SDG Workshop 2021, 2022, pp. 421–428.
- [9] R. M. Mahamood, T.-C. Jen, S. A. Akinlabi, S. Hassan, and E. T. Akinlabi, "9 Tribology of additively manufactured titanium alloy for medical implant," in *Tribology of Additively Manufactured Materials*, P. Kumar, M. Misra, and P. L. Menezes, Eds. Elsevier, 2022, pp. 267– 288.

- [10] Z. M. Jin, J. Zheng, W. Li, and Z. R. Zhou, "Tribology of medical devices," *Biosurface and Biotribology*, vol. 2, no. 4, pp. 173–192, 2016, doi: https://doi.org/10.1016/j.bsbt.2016.12.001.
- [11] K. Holmberg and A. Erdemir, "Influence of tribology on global energy consumption, costs and emissions," *Friction*, vol. 5, no. 3, pp. 263–284, 2017, doi: 10.1007/s40544-017-0183-5.
- [12] R. J. Shah, M. Woydt, N. Huq, and A. Rosenkranz, "Tribology meets sustainability," *Ind. Lubr. Tribol.*, vol. 73, no. 3, pp. 430–435, 2021, doi: 10.1108/ilt-09-2020-0356.
- [13] X. Fu, L. Sun, X. Zhou, Z. Li, and T. Ren, "Tribological Study of Oil-Miscible Quaternary Ammonium Phosphites Ionic Liquids as Lubricant Additives in PAO," *Tribol. Lett.*, vol. 60, no. 2, p. 23, 2015, doi: 10.1007/s11249-015-0596-0.
- [14] M. Woydt *et al.*, "Tribology in Germany Wear protection and sustainability as cross-sectional challenges An expert study by the Gesellschaft für Tribologie e.V.," 2021. [Online]. Available: https://www.itctribology.net/en/tribology-wordwide/tribology-impact-references/.
- [15] J. C. Spear, B. W. Ewers, and J. D. Batteas, "2D-nanomaterials for controlling friction and wear at interfaces," *Nano Today*, vol. 10, no. 3, pp. 301–314, 2015, doi: https://doi.org/10.1016/j.nantod.2015.04.003.
- [16] Q. Huang, X. Shi, Y. Xue, K. Zhang, and C. Wu, "Recent progress on surface texturing and solid lubricants in tribology: Designs, properties, and mechanisms," *Mater. Today Commun.*, vol. 35, p. 105854, 2023, doi: https://doi.org/10.1016/j.mtcomm.2023.105854.
- [17] T. Naveed, R. Zahid, R. A. Mufti, M. Waqas, and M. T. Hanif, "A review on tribological performance of ionic liquids as additives to bio lubricants," *Proc. Inst. Mech. Eng. Part J J. Eng. Tribol.*, vol. 235, no. 9, pp. 1782–1806, 2021, doi: 10.1177/1350650120973805.
- [18] A. Z. Khamidullaevna, "Improve The Physico Chemical Properties Of Hydraulic Oils Way Of Introduction Of Additives," Am. J. Eng. Technol., 2021, doi: 10.37547/tajet/Volume03Issue12-01.
- [19] S. M. Bidak, M. I. Nessim, F. I. El-Dossoki, D. A. Ismail, H. A. Mohammed, and A. A. M. El-Bassoussi, "Synthesis, Evaluation of asymmetric dicationic Ionic Liquids and studying their efficiency for Egyptian Base Oil improvement," *Egypt. J. Chem.*, 2022, doi: 10.21608/ejchem.2022.146789.6377.
- [20] V. S. Sharma, N. Doerr, A. Erdemir, and P. B. Aswath, "Interaction of phosphonium ionic liquids with borate esters at tribological interfaces," *RSC Adv.*, vol. 6, no. 58, pp. 53148–53161, 2016, doi: 10.1039/c6ra11822d.
- [21] G. S. Goindi, P. Sarkar, A. D. Jayal, S. N. Chavan, and D. Mandal, "Investigation of ionic liquids as additives to canola oil in minimum quantity lubrication milling of plain medium carbon steel,"

Int. J. Adv. Manuf. Technol., vol. 94, no. 1, pp. 881–896, 2018, doi: 10.1007/s00170-017-0970-1.

- [22] J. Qu et al., "Antiwear Performance and Mechanism of an Oil-Miscible Ionic Liquid as a Lubricant Additive," ACS Appl. Mater. \& Interfaces, vol. 4, no. 2, pp. 997–1002, 2012, doi: 10.1021/am201646k.
- [23] S. Bhaumik, V. Paleu, R. Pathak, R. Maggirwar, J. K. Katiyar, and A. K. Sharma, "Tribological investigation of r-GO additived biodegradable cashew nut shells liquid as an alternative industry lubricant," *Tribol. Int.*, vol. 135, pp. 500–509, 2019, doi: https://doi.org/10.1016/j.triboint.2019.03.007.
- [24] R. Monge *et al.*, "Ionic liquids as an additive in fully formulated wind turbine gearbox oils," *Wear*, vol. 328–329, pp. 50–63, 2015, doi: https://doi.org/10.1016/j.wear.2015.01.041.
- [25] Y. Zhou, J. Dyck, T. W. Graham, H. Luo, D. N. Leonard, and J. Qu, "Ionic Liquids Composed of Phosphonium Cations and Organophosphate, Carboxylate, and Sulfonate Anions as Lubricant Antiwear Additives," *Langmuir*, vol. 30, no. 44, pp. 13301–13311, 2014, doi: 10.1021/la5032366.
- [26] S. Yang, J. S. S. Wong, and F. Zhou, "Ionic Liquid Additives for Mixed and Elastohydrodynamic Lubrication," *Tribol. Trans.*, vol. 61, no. 5, pp. 816–826, 2018, doi: 10.1080/10402004.2018.1426802.
- [27] A. E. Somers, B. Khemchandani, P. C. Howlett, J. Sun, D. R. MacFarlane, and M. Forsyth, "Ionic Liquids as Antiwear Additives in Base Oils: Influence of Structure on Miscibility and Antiwear Performance for Steel on Aluminum," ACS Appl. Mater. \& Interfaces, vol. 5, no. 22, pp. 11544– 11553, 2013, doi: 10.1021/am4037614.
- [28] V. Totolin, I. Minami, C. Gabler, and N. Dörr, "Halogen-free borate ionic liquids as novel lubricants for tribological applications," *Tribol. Int.*, vol. 67, pp. 191–198, 2013, doi: https://doi.org/10.1016/j.triboint.2013.08.002.
- [29] B. Khemchandani, A. Somers, P. Howlett, A. K. Jaiswal, E. Sayanna, and M. Forsyth, "A biocompatible ionic liquid as an antiwear additive for biodegradable lubricants," *Tribol. Int.*, vol. 77, pp. 171–177, 2014, doi: https://doi.org/10.1016/j.triboint.2014.04.016.
- [30] I. Otero, E. R. López, M. Reichelt, M. Villanueva, J. Salgado, and J. Fernández, "Ionic Liquids Based on Phosphonium Cations As Neat Lubricants or Lubricant Additives for a Steel/Steel Contact," ACS Appl. Mater. \& Interfaces, vol. 6, no. 15, pp. 13115–13128, 2014, doi: 10.1021/am502980m.
- [31] J. Grace, S. Vysochanska, J. Lodge, and P. Iglesias, "Ionic Liquids as Additives of Coffee Bean Oil in Steel-Steel Contacts," *Lubricants*, vol. 3, no. 4, pp. 637–649, 2015, doi:

10.3390/lubricants3040637.

- [32] A. E. Jiménez and M.-D. Bermúdez, "Ionic Liquids as Lubricants of Titanium–Steel Contact," *Tribol. Lett.*, vol. 33, no. 2, pp. 111–126, 2009, doi: 10.1007/s11249-008-9396-0.
- [33] M. Ahmed, M. Nessim, A. M., Bassoussi, Salem, and Attia, "THE EFFECT OF SOME BENZOTHIAZOLE DERIVATIVES AS ANTIOXIDANTS FOR BASE STOCK," Int. J. Curr. Res., vol. 5, pp. 1111–1117, 2013.
- [34] M. I.NESSIM, D. I. OSMAN1, E.-S. K. ATTIA, E. A.AHME, and H. A. MOHAMMED, "THE ROLE OF 5-(4-ALKOXYBENZYLIDENE)-2-THIOXO-4-OXO-1, 3-THIAZOLIDINE AS ANTIOXIDANTS FOR EGYPTIAN LUBE OIL BASE STOCK," *Int. J. Curr. Res. Chem. Pharm. Sci.*, vol. 2, no. 2, pp. 80–93, 2017.
- [35] H. A. Mohammed, M. I. Nessim, A. A. M. El-Bassoussi, D. I. Osman, and M. K. Zahran, "Novel heterocyclic compounds as antioxidants for Egyptian base stock," *Life Sci. J.*, vol. 11, no. 9, pp. 823–835, 2014.
- [36] M. I. Nessim, A. A. El-Bassoussi, M. Y. El-kady, N. Hassan, and S. M. B. Bidak, "Synthesis and Evaluation of Some Thiazolidinone Derivatives as Antioxidants for Local Base Stock," 2017.
- [37] J. S. Basta, A. A. El-Bassoussi, A. A. Salem, M. I. Nessim, M. H. Ahmed, and S. K. Attia, "Preparation and evaluation of some benzimidazole derivatives as antioxidants for local base oil," *Egypt. J. Pet.*, vol. 26, no. 4, pp. 933–941, 2017, doi: https://doi.org/10.1016/j.ejpe.2016.10.001.
- [38] S. Rizk, s. K. Attia, D. Osman, and M. Nessim, "Synthesis and Applications of Pyridazinones for Base Oil Improvement," *Egypt. J. Chem.*, vol. 60, pp. 129–146, 2017, doi: 10.21608/ejchem.2017.675.1015.
- [39] H. A. Mohammed, S. K. Attia, M. I. Nessim, M. E. Shaaban, and A. A. M. El-Bassoussi, "Studies on some thiazolidinones as antioxidants for local base oil," *Egypt. J. Chem.*, vol. 62, no. 7, pp. 1619–1634, 2019, doi: https://doi.org/10.21608/EJCHEM.2019.6662.1560.
- [40] A. Ashmawy, E. M. Elnaggar, M. E. L. NAGGAR, and M. I.NESSIM, "Studies on the Additive Performance of AZO Phenol Liquid Crystal as Antioxidant for Base Stocks," *Int. J. Innov. Res. Sci. Eng. Technol.*, vol. 6, pp. 358–366, 2017, doi: 10.15680/IJIRSET.2017.0601169.
- [41] A. Ashmawy, M. Nessim, E. M. Elnaggar, and D. Osman, "Preparation and evaluation of some novel liquid crystals as antioxidants," *Mol. Cryst. Liq. Cryst.*, vol. 643, pp. 188–198, 2017, doi: 10.1080/15421406.2016.1264240.
- [42] A. M. Ashmawy, S. K. Attia, M. I. Nessim, E. sayed M. Elnaggar, and A. A. El-Bassoussi, "Study on some azo liquid crystals as antioxidants for local base oil," *Mol. Cryst. Liq. Cryst.*, vol. 668, no.

1, pp. 78–90, 2018, doi: 10.1080/15421406.2018.1560917.

- [43] A. Ashmawy, M. Nessim, D. Osman, and E. S. Elnaggar, "Preparation and evaluation of some newly liquid crystal as antioxidant for base stocks," *Iran. Chem. Commun.*, vol. 7, no. Issue 3, pp. 160–229, Serial No. 24, pp. 196–205, 2019, doi: 10.30473/icc.2018.4825.
- [44] M. M. Barakat, M. A. Deyab, M. I. Nessim, S. S. A. El-Rehim, and Q. Mohsen, "The controlling role of new imidazole-based ionic liquids on the corrosion rate of steel rebars in the cement pore solution," *J. Mol. Liq.*, vol. 329, p. 115442, 2021, doi: https://doi.org/10.1016/j.molliq.2021.115442.
- [45] J.-C. Chang *et al.*, "Synthesis and characterization of dicationic ionic liquids that contain both hydrophilic and hydrophobic anions," *Tetrahedron*, vol. 66, no. 32, pp. 6150–6155, 2010, doi: https://doi.org/10.1016/j.tet.2010.05.105.
- [46] M. I. Nessim, M. T. Zaky, and M. A. Deyab, "Three new gemini ionic liquids: Synthesis, characterizations and anticorrosion applications," J. Mol. Liq., vol. 266, pp. 703–710, 2018, doi: https://doi.org/10.1016/j.molliq.2018.07.001.
- [47] F. I. El-Dib, S. M. Ahmed, D. A. Ismail, and D. E. Mohamed, "Synthesis and Surface Properties of Novel N-Alkyl Quinoline-Based Cationic Gemini Surfactants," *J. Dispers. Sci. Technol.*, vol. 34, no. 4, pp. 596–603, 2013, doi: 10.1080/01932691.2012.683979.
- [48] M. I. Nessim, M. M. Osman, and D. A. Ismail, "Surface-active properties of new cationic gemini surfactants with cyclic spacer," J. Dispers. Sci. Technol., vol. 39, no. 7, pp. 1047–1055, 2018, doi: 10.1080/01932691.2017.1381916.
- [49] ASTM, "Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration," American, ASTM D664-18e2, 2018. [Online]. Available: https://www.astm.org/Standards/D664.htm.
- [50] "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)." [Online]. Available: https://www.astm.org/d0445-21e02.html.
- [51] "Standard Test Method for Foaming Characteristics of Lubricating Oils." [Online]. Available: https://www.astm.org/d0892-18e01.html.
- [52] S. D. Wettig and R. E. Verrall, "Thermodynamic Studies of Aqueous m-s-m Gemini Surfactant Systems," J. Colloid Interface Sci., vol. 235, no. 2, pp. 310–316, 2001, doi: https://doi.org/10.1006/jcis.2000.7348.
- [53] R. Zana, "Dimeric (Gemini) Surfactants: Effect of the Spacer Group on the Association Behavior in Aqueous Solution," J. Colloid Interface Sci., vol. 248, no. 2, pp. 203–220, 2002, doi:

https://doi.org/10.1006/jcis.2001.8104.

- [54] L. Grosmaire, M. Chorro, C. Chorro, S. Partyka, and R. Zana, "Alkanediyl-α,ωbis(dimethylalkylammonium bromide) surfactants: 9. Effect of the spacer carbon number and temperature on the enthalpy of micellization," *J. Colloid Interface Sci.*, vol. 246, pp. 175–181, 2002, doi: 10.1006/jcis.2001.8001.
- [55] E. Alami, H. Levy, R. Zana, and A. Skoulios, "Alkanediyl-.alpha.,.omega.bis(dimethylalkylammonium bromide) surfactants. 2. Structure of the lyotropic mesophases in the presence of water," *Langmuir*, vol. 9, no. 4, pp. 940–944, 1993, doi: 10.1021/la00028a011.
- [56] H. Nakahara, A. Nishino, A. Tanaka, Y. Fujita, and O. Shibata, "Interfacial behavior of gemini surfactants with different spacer lengths in aqueous medium," *Colloid Polym. Sci.*, vol. 297, 2019, doi: 10.1007/s00396-018-4459-8.
- [57] S. M. Ahmed, T. T. Khidr, and D. A. Ismail, "Effect of gemini surfactant additives on pour point depressant of crude oil," J. Dispers. Sci. Technol., vol. 39, no. 8, pp. 1160–1164, 2018, doi: 10.1080/01932691.2017.1385483.
- C. E. El shafiee et al., "Application of asymmetric dicationic ionic liquids for oil spill remediation [58] J. sea water." Arab. Chem., vol. 14, no. 5, p. 103123, 2021, doi: in https://doi.org/10.1016/j.arabjc.2021.103123.
- [59] A. Y. El-Naggar *et al.*, "Oxidation stability of lubricating base oils," *Pet. Sci. Technol.*, vol. 36, no. 3, pp. 179–185, 2018, doi: 10.1080/10916466.2017.1403450.
- [60] K. Lubrication, "Foaming characteristics of gear oil." Edition.
- [61] T. C. Prolic and A. Lepusic, "Effect of foaming on the antiwear properties of lubricating oils," *Goriva i Maz.*, vol. 51, no. 1, p. 38, 2012.