

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/



Synthesis, Evaluation of asymmetric dicationic Ionic Liquids and studying their efficiency for Egyptian Base Oil improvement



Sameh M Bidak¹, Maher I Nessim^{*2} Farid I. El-Dossoki³, Dina A. Ismail⁴, Hoda A. Mohammed², ^{CrossMark} Ali A. M. El-Bassoussi²

¹ Laboratories Department, United Gas Derivative Company, Port Said, Egypt. ² Analysis and evaluation Department, Egyptian Petroleum Research Institute, Cairo, Egypt.

³ Chemistry Department, Faculty of Science, Port Said University, Port Said, Egypt.

⁴ Petrochemical Department, Egyptian Petroleum Research Institute, Cairo, Egypt.

Abstract

work, three asymmetric dicationic ionic liquids, namely, 1-(2-(1-decyl-1H-imidazolium-3-yl)ethyl)-4-In this methylpyridinium bromide (IL101), 1-(5-(1-decyl-1H-imidazolium-3-yl)pentyl)-4-methylpyridinium bromide (IL102), and 1-(10-(1-decyl-1H-imidazolium-3-yl)decyl)-4-methyl-pyridinium bromide (IL₁₀₃) were synthesized. Their structures were confirmed and characterized via, elemental analysis, Fourier transform infra-red spectroscopy and proton nuclear magnetic resonance. The surface properties of these ionic liquids, surface tension, critical micelle concentration, effectiveness, maximum surface excess, and minimum surface area, were investigated with different concentrations at 25°C. Standard free energies of micellization and adsorption were obtained. They were studied and tested as base oil improvers, especially oxidation stability, (through studying the change in total acid number [TAN] and viscosity), and foaming characteristics. The efficiency of these compounds as base oil improvers is ranked as follows, $IL_{103} > IL_{102} > IL_{101}$.

Keywords: Ionic liquid; Surface parameters; Base oil; Oxidation stability; Total acid number; Foaming, Spectroscopy.

1. Introduction

In lubricant applications there is always a drive to reduce emissions, increase durability, and increase service intervals, as well as to reduce friction and thus energy use. To meet these challenges, lubricants must be always improved. These improvements can also lead to technological advances by enabling the use of new materials for a particular application [1].

Generally, there are three different base oils used in the formulation of lubricating oil, these are; mineral, bio-based (natural) and synthetic base oils [2, 3].

Mineral base oils used in engineering machines were derived from one of the distillation fractions of crude oil containing (C20-C50) hydrocarbons. However, the base oil will be predominantly isoparaffinic and naphthenic hydrocarbons if the fraction boiling is under 723 K together with a few percent of mono aromatic hydrocarbons [3, 4].

Lubricants based on biological sources are able to adhere to metal surfaces, enabling improved boundary lubrication. In a contrary, their drawbacks are associated with their high sensitivity to oxidation, hydrolytic instability and high pour points [3, 5-7].

Many synthetic lubricants have been produced and some of them have been applied such as poly-alpha olefins (PAOs). Many examples of synthetic oils are; synthetic hydrocarbon polymers, poly-phenyl ethers, halogenated hydrocarbons, carboxylate esters, aliphatic esters, polyol esters, phosphate esters and poly-alkylene glycols [8-11].

The prolonged use of lubricants alone on the contact surfaces results in ramification to corrosion and wear, which directly affects the engine efficiency. Oxidation is considered as the most important chemical phenomenon in lubricating oils [12, 13]. Total Acid Number (TAN) is one of tools used for measuring of acidic matter remaining in the oil because of the degradation process that occurred. Also, foam control is a very important factor in froth flotation of ores and other minerals, and the mechanisms of foam destruction in froth flotation are similar to those encountered in antifoam applications [14, 15].

Ionic liquids (ILs) are a class of organic molten salts consisting of only cations and anions [16]. ILs have extensive applications because of their unique

Receive Date: 25 June 2022, Revise Date: 14 August 2022, Accept Date: 30 August 2022. https://doi.org/10.21608/ejchem.2022.146789.6377

^{*}Corresponding author e-mailmaherni@yahoo.com; (Maher I Nessim).

^{©2023} National Information and Documentation Center (NIDOC)

physicochemical characteristics such as negligible vapor pressure, high thermal stability, larger surface tensions, higher shear viscosities, high thermal conductivity, wide electrochemical window and low melting point, etc. [17]. Compared to traditional monocationic ionic liquids, dicationic ionic liquids (DILs), especially asymmetrical dicationic ionic liquids (ADILs), have shown to possess superior physiochemical properties in the field of volatility and thermal stability [18]. Therefore, they can be used as for many applications including dyesensitized cells, organic synthesis, anti-corrosive additives, coatings or antioxidants, lubricants and lubricant additives [19].

Findings from several studies conducted in the past years say that the addition of engine oil additives act as defoamers [14,15,20], viscosity improvers, pour-point depressants, anti-wear additives, extreme pressure additives, etc. Thus, engine oil additives could serve as potential solution to the problem of reduced efficiencies [14].

The use of additives is very important. Their selection is based on the ability of them to reduce friction and wear, controlling viscosity, improving viscosity index, resist corrosion and oxidation [15,20-22], increase oil lifetime through prevention, and monitoring of oil degradation. Not only the oil quality is the main consideration but also the economic considerations are important. e.g., the cost of oil can be very expensive for the huge machinery that holding several thousand liters of lubricating oil [21]. Different examples of common additives include dispersants, antioxidants, friction modifiers, anti-wear agents, detergents and viscosity index (VI) improvers. The most available constituents of modern engine oils are discussed in many literatures [23-25].

In our previous work we synthesized and used different heterocyclic compounds, [26-32], azophenols, [33] and azo-liquid crystals [34-36] for base oil improvement such as antioxidants, viscosity improvers and pour point depressants. In this present work we synthesized and studied the effect of some asymmetric dicationic ionic liquids as antioxidants, viscosity improvers and anti-foams for tested Egyptian hydro finished base oil.

2. Experimental

2.1. Materials and Methodology

i- physicochemical characteristics of delivered Base oil, (Co-operation Petroleum Company) It is carried out according to ASTM standard test methods, Table 1.

ii- Chemicals and solvents, purchased from international chemical companies, were used without further purification. Acetonitrile (anhydrous), ethyl acetate (99.5%), absolute ethyl alcohol, 1bromodecane (98%), 1H-imidazole (99%), petroleum ether (40–60) (98%), and potassium hydroxide (97%), Merck. 4-Methyl pyridine (99%), 1,2dibromoethane (99%), 1,5-dibromopentane (99%), 1,10-dibromodecane (99%), Alfa Aesar.

iii- Synthesis of dicationic ionic liquids IL₁₀₁₋₁₀₃ Steps of synthesis were illustrated as follows:

Compound (I) was prepared previously [37]. In a conical flask, 1H-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 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.

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.



Equation 1: Preparation of 1-decyl-1H-imidazole (I)

Test	Result	Standard Test Method	
Density @ 15.56 °C, g /cm3	0.8807	ASTM D – 1298	
Pour Point, °C	0	ASTM D – 97	
Viscosity @ 40 °C	165.33	ASTM D – 445	
@ 100 °C	15.56	ASTM D – 445	
Viscosity Index (VI)	95	ASTM D – 2270	
Total Acid Number (TAN)	0.061	ASTM D – 664	
Foaming Characteristics at			
50°C,		ASTM D – 892	
Foaming Volume (ml)	170		
Collapse Time (s)	480		
Sulfur Content, (wt.%)	0.41	ASTM D – 4294	
Color	3.5	ASTM D – 1500	
Copper Corrosion	1a	ASTM D – 130	
Flash Point, °C	220	ASTM D – 92	
Ash Content, (wt.%)	0.003	ASTM D – 482	
Wax Content, wt.%	1.6	UOP - 46	
Saturate Content, wt.%	54.36		
Aromatic Content, wt.%	45.54		
Molecular weight	321.23		

Table 1 Physicochemical properties of the Base oil

Compounds [101, 102 and 103] were prepared by stirring 4-methyl pyridine (0.01 mol) and dibromo alkanes, (1,2-dibomoethane, 1,6-dibromohexane and

White precipitate was afforded by filtration and recrystallized from petroleum ether 40–60, equation 2, [38].



Equation 2: Preparation of 1-(n-bromoalkyl)-4-methylpyridin-1-ium bromide

101; n = 2, 1-(2-bromoethyl)-4-methylpyridin-1-ium bromide 102; n = 5, 1-(5-bromopentyl)-4-methylpyridin-1-ium bromide 103; n = 10, 1-(10-bromodecyl)-4-methylpyridin-1-ium bromide

Synthesis of Ionic Liquids $IL_{101-103}$: These compounds were synthesized by refluxing compound (I) (0.01 mol.) with compounds 101-103, (0.01 mol.) in 50 ml acetonitrile for 12 h at 80 °C. Purification of

Metrohm Titrando 905 potentiometer, stirrer 801 and electrode model 6.0229.010. Instrument parameters used according to Metrohm Application Bulletin AB-404/2e.



Equation 3: Preparation of IL₁₀₁₋₁₀₃

$$\label{eq:linear} \begin{split} & IL_{101}: 1-(2-(1-decyl-1H-imidazol-3-ium-3-yl) ethyl)-4-methylpyridin-1-ium bromide. \\ & IL_{102}: 1-(5-(1-decyl-1H-imidazol-3-ium-3-yl) pentyl)-4-methylpyridin-1-ium bromide. \\ & IL_{103}: 1-(10-(1-decyl-1H-imidazol-3-ium-3-yl) decyl)-4-methylpyridin-1-ium bromide. \end{split}$$

The products was carried out via evaporation of acetonitrile under vacuum, equation 3, [39].

The synthesized compounds were characterized using the conventional tools of analysis, Elemental

analysis (Micro analytical center, Cairo, Egypt using Elementary Viro El Microanalysis), FT-IR spectrophotometer (Model 960 Mooog, ATI Mattson

Infinity Series, USA, Cairo, Egypt) and 1H-NMR spectra (Bruker High Performance Digital 1H-NMR

Spectrometer Advance III 400 MHz using DMSO as solvent.

2.2. Surface tension measurements:

Surface tension measurements were obtained using a Du Noüy tensiometer with a platinum ring. Freshly prepared aqueous solutions of asymmetric IL $_{101-103}$ bola surfactants were measured over a concentration range of 0.01–0.000001 M/L at 25°C. The surface tension of double distilled water was measured to calibrate instruments, 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 [40,41].

2.3. Total Acid Number:

This test underwent for the base oil without and with the additives via ASTM D664 [42], using

2.4. Viscosity:

According to ASTM D445 [43], viscosities of the samples without and with the additives were

Table 2: Elemental analysis of the ionic liquids (IL₁₀₁₋₁₀₃).

measured using CT-1000 CANON oil bath, Cannon-Fenske viscometers size 150, and Kohler thermometer instrument.

2.5. Foaming test:

foaming characteristics were measured for the blank sample and the three samples after adding the additives using ASTM D892 [44] (Petrotest DP water bath and ZEAL DM3A gas meter)

3. Results and discussion

3.1. Characterization of IL101-103

3.1.1. Elemental analysis:

Data tabulated in Table 2 revealed that the calculated values are in good matching with the observed ones.

3.1.2. FT-IR:

Data recorded in table (3) and charts 1-3 illustrated the following:

TT //	C%		H%		N%		Br%		Mol.
IL#	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Wt.
IL101	51.55	51.34	7.21	7.19	8.59	8.64	32.66	32.82	489
IL102	54.24	54.08	7.78	7.82	7.91	8.05	30.07	29.35	531
IL103	57.90	57.68	8.55	8.63	6.99	7.04	26.57	26.64	602

- In the FT-IR spectra of compounds (IL₁₀₁₋₁₀₃), the aromatic stretching vibrations bands of benzene C-H bonds are observed in the range of 3128-3039 cm-1. Stretching vibrations bands of aromatic C=C are observed in the regions of 1512, 1511 and 1517 cm-1 respectively.
- N-H broad stretching bands, appeared at 3423, 3425 and 3412 cm-1, for (IL₁₀₁₋₁₀₃) are attributed to the presence of the carbene proton in the form of NH+ in imidazole ring [35].
- Aromatic C-H stretching bands appeared at 3089-3046, 3090(broad), and 3128-3039 cm-1 respectively.
- Aliphatic C-H (stretching) bands appeared at 2925-2856, 2924-2854 and 2926-2856 cm-1.
- All the specific imidazole zone bands were obtained precisely [39].

Chart 1: IR spectrum of IL₁₀₁



	(
IL	NH+	CH Ar	CH Aliph atic	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 101	3423 broad	3089- 3046	2925, 2856	1512	1462	1569	1462- 1378	1285- 1183	758	1040-948	830, 758	628
IL 102	3425 broad	3090 broad	2924- 2854	1511	1462	1565	1462- 1373	1292- 1231	731	1081-913	830, 731	626
IL 103	3412 broad	3128- 3039	2926- 2856	1517	1463	1564	1463- 1372	1308- 1240	754	1044-931	831-754	631

Chart 2: IR spectrum of IL₁₀₂



Chart 3: IR spectrum of IL103



3.1.3. ¹H-NMR:

Table 4 and charts 4-6 shows the obtained results of 1 H-NMR for prepared compounds IL₁₀₁₋₁₀₃.





Egypt. J. Chem. 66, No. 5 (2023)



Chart 6: NMR spectrum of IL₁₀₃



3.2. Surface activity

The critical micellar concentrations (cmc) determined from the surface tension measurements are given in Table 5.

The surface excess concentration (Γ max) and minimum area per molecule at the air–water interface (Amin) determined from surface tension data using Equations (i and ii) [45-47] are given in Table 5.

$$\Gamma_{\text{max}} = -1/n\text{RT} (d\gamma / d\ln C)$$
(i)

$$A_{\text{min}} = 10^{16} / N_A \Gamma_{\text{max}}$$
(ii)

Where R is gas constant, T is temperature, γ is the surface tension, and N_A is Avogadro's number. The constant n takes the values 2 for an ionic surfactant where the surfactant ion and the counter ion are univalent and n = 3 for a dimeric surfactant made up

of a divalent surfactant ion and two univalent counter ions, in the absence of a swamping electrolyte [46]. Hence a value of n = 3 was used in Eq. (i) for the present ionic dimeric surfactant system.

The results of surface tension measurements are shown in Fig. 2. Table 5 lists the values of CMC, surface tension at CMC (γ_{CMC}), Γ_{max} , A_{min} , and P_{C20} of IL₁₀₁₋₁₀₃.

As listed in Fig. 2, these asymmetric ionic liquids have the same head groups and hydrophobic chains, but differs in spacer chain lengths. The spacer should, Therefore, be the principal factor determining differences in surface properties.

As shown in Table 5, these compounds have low CMC values. They formed compact micelles due to strong hydrophobic interaction between multiple hydrocarbon chains. We noticed that, with the increase in spacer chain length, γ_{CMC} does not show a marked difference with change in the spacer length (m = 2, 5 or 10), and the CMC values decrease for the di cationic ionic liquids.

The area occupied per molecule (A_{min}) decreased with the increase in spacer chain length, which will improve the flexibility of the molecular and reduce the backbone rigid and pack more tightly at the

Table 4: Chemical Shift (δ ppm) for compound IL₁₀₃₋₁₀₅.

air/water contact, which causes the decrease in Amin. The spacer may penetrate the hydrophobic core. The saturation surface excess concentration (Γ_{max}) increases as A_{min} decreases. Due to the decrease in repulsion between the oriented ionic heads at the interface when the spacer bend more to the hydrophobic phase, adsorbing as a folded, wicket-like conformation [48].



Figure 1: Surface tension isotherms of IL101-103 at 25 °C

	Proton type	e (δ ppm)										
Compound	a	b	с	d	e	f	g	h	Ι	j	k, k [/]	L
IL ₁₀₁	9.31 (s)	9.16 (d)	8.08 (d)	7.83 (d)	7.59 (d)	5.25 (1) 4.19 (t)	2.67 (s)	1.79 (m)	1.23 (s)	0.86	9.31 (s)
IL ₁₀₂	9.33 (s)	9.04 (d)	8.02 (d)	7.97 (d)	7.24 (d)	4.59 (1) 4.21 (t)	2.62 (s)	1.96 (m)	1.79 (m)	1.70 (m) 1.22 (s)	0.84 (t)
IL ₁₀₃	9.36 (s)	9.01 (d)	8.00 (d)	7.86 (d)	7.75 (s)	4.58 (1) 4.18 (t)	2.61 (s)	1.86 (m)	1.78 (m)	1.76 (m) 1.23 (s)	0.84 (t)

$-i$ and S_{*} but face that annound on the synthesized surfact and s is the set	Table 5: Surface	parameters of	the synthesized	surfactants	[IL101-103]
--	------------------	---------------	-----------------	-------------	-------------

CMC mol./L	γ _{смс} mN/m	π_{CMC} mN/m	P_{c20}	$\Gamma_{\rm max} x 10^{10}$ mol./ cm2	$\begin{array}{c} A_{min} \\ nm^2 \end{array}$	∆G° mic KJ/mol	∆G° ads KJ/mol
6 x10 ⁻⁴	32	40	7x10 ⁻⁵	1.359	1.222	-18.381	-47.824
1 x10 ⁻⁴	31	41	1.2x10 ⁻⁶	1.372	1.210	-22.823	-52.703
5 x10 ⁻⁵	33	39	8x10 ⁻⁶	1.452	1.144	-24.540	-51.412
	CMC mol./L 6 x10 ⁻⁴ 1 x10 ⁻⁴ 5 x10 ⁻⁵	$\begin{array}{c} \text{CMC} & \gamma_{\text{CMC}} \\ \text{mol./L} & \text{mN/m} \\ \hline 6 \text{ x10}^{-4} & 32 \\ 1 \text{ x10}^{-4} & 31 \\ 5 \text{ x10}^{-5} & 33 \end{array}$	$\begin{array}{c} {\rm CMC} \\ {\rm mol./L} \end{array} & \begin{array}{c} \gamma_{\rm CMC} \\ {\rm mN/m} \end{array} & \begin{array}{c} \pi_{\rm CMC} \\ {\rm mN/m} \end{array} \\ \\ 6 \ x10^{-4} & 32 & 40 \\ \\ 1 \ x10^{-4} & 31 & 41 \\ \\ 5 \ x10^{-5} & 33 & 39 \end{array}$	CMC mol./L γ_{CMC} mN/m π_{CMC} mN/m P_{c20} 6×10^{-4} 3240 7×10^{-5} 1×10^{-4} 3141 1.2×10^{-6} 5×10^{-5} 3339 8×10^{-6}	CMC mol./L γ_{CMC} mN/m π_{CMC} mN/m P_{c20} $\Gamma_{max} x 10^{10}$ mol./ cm2 $6 x 10^{-4}$ 32 40 $7 x 10^{-5}$ 1.359 $1 x 10^{-4}$ 31 41 $1.2 x 10^{-6}$ 1.372 $5 x 10^{-5}$ 33 39 $8 x 10^{-6}$ 1.452	CMC mol./L γ_{CMC} mN/m π_{CMC} mN/m P_{c20} $\Gamma_{max} x 10^{10}$ mol./ cm2 A_{min} nm2 $6 x 10^{-4}$ 32 40 $7x 10^{-5}$ 1.359 1.222 $1 x 10^{-4}$ 31 41 $1.2x 10^{-6}$ 1.372 1.210 $5 x 10^{-5}$ 33 39 $8x 10^{-6}$ 1.452 1.144	CMC mol./L γ_{CMC} mN/m π_{CMC} mN/m P_{c20} $\Gamma_{max}x10^{10}$ mol./ cm2 A_{min} nm2 ΔG° mic KJ/mol $6 x10^4$ 32 40 $7x10^{-5}$ 1.359 1.222 -18.381 $1 x10^4$ 31 41 $1.2x10^{-6}$ 1.372 1.210 -22.823 $5 x10^{-5}$ 33 39 $8x10^{-6}$ 1.452 1.144 -24.540

The difference between the surface tension of IL₁₀₁₋₁₀₃ at their CMC and that of pure water is termed "effectiveness" (π_{CMC}): $\pi_{CMC} = \gamma 0 - \gamma$

where $\gamma 0$ is the surface tension of the pure water and γ is the surface tension of the solution at CMC [49]. The effectiveness of the IL₁₀₁₋₁₀₃ ranged between 39 and 41 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 (P_{C20}) : The P_{C20} values were determined in Table (5). P_{C20} is the bulk surfactant

concentration needed to reduce the surface tension of the solvent by an arbitrary 20 mNm-1.

This value commonly characterized the efficiency of a surfactant to lower surface tension. Values of C20 showed that IL₁₀₁₋₁₀₃ indicated that they have great efficiency in reducing surface tension of water and consequently, have high surface activity. Standard free energy of micellization (ΔG°_{mic}), and standard free energy of adsorption (ΔG°_{ads}):

 ΔG°_{mic} is calculated as ΔG° mic = RT ln CMC.

 ΔG°_{mic} for the synthesized IL₁₀₁₋₁₀₃ surfactant were always negative values, indicating that micellization was a spontaneous process. The general trend of - ΔG°_{mic} increase with increasing the distance between

the two heads groups (spacer), i.e., it became less negative. This indicates that increasing in the spacer length and hydrophobicity favor the micellization process.

6:	Variation	of	total	acid	number	(mg	KOH/g)	without	and	with	IL 101-103
ala		II	Ls Conc.		Time interval	ls (hrs.)					<u> </u>
pie		pp	pm		24	48		72	96		
oil k (wit	hout additive)	0.	.061		0.2621	0.4	636	0.7056	0	.9130	
		20	00		0.1935	0.3	145	0.3752	0	.4032	
		40	00		0.0826	0.1	895	0.2670	0	.3545	
		60	00		0.0408	0.0	605	0.0934	0	.1747	
		20	00		0.1915	0.2	580	0.3225	0	.3896	
		40	00		0.0625	0.1	613	0.2419	0	.3230	
		60	00		0.0403	0.0	504	0.0835	0	.1512	
		20	00		0.0615	0.1	126	0.1895	0	.2923	
		40	00		0.0346	0.0	406	0.0797	0	.1613	
		60	00		0.0302	0.0	346	0.0635	0	.0775	
	6: ole oil k (wit	6: Variation ble oil k (without additive)	6: Variation of ble II pp oil 0. 0. k (without additive) 0. 20 40 60 20 40 60 20 40 60 20 40 60 20 40 60 60 40 60 60 40 60 60 40 60 60 40 60 60	6: Variation of total ble ILs Conc. ppm oil 0.061 k (without additive) 200 400 600 200 400 600 200 400 600 200 400 600 200 400 600 600 600	6:VariationoftotalacidbleILs Conc. ppmoil k (without additive) 0.061 200 400 600 200 400 600 200 400 600 200 400 600 400 600 600 200 600 600	6: Variation of total acid number ble ILs Conc. ppm Time interval ppm 24 oil k (without additive) 0.061 0.2621 200 0.1935 400 0.0826 600 0.0408 200 0.1915 400 0.0625 600 0.0403 200 0.0615 400 0.0346 600 0.0302	6: Variation of total acid number (mg ble ILs Conc. Time intervals (hrs.) ppm 24 48 oil 0.061 0.2621 0.4 k (without additive) 200 0.1935 0.3 400 0.0826 0.1 600 0.0408 0.0 200 0.1915 0.2 400 0.0625 0.1 600 0.0403 0.0 200 0.0615 0.1 400 0.0625 0.1 600 0.0346 0.0	6: Variation of total acid number (mg KOH/g) ble ILs Conc. ppm Time intervals (hrs.) ppm 1 24 48 oil (without additive) 0.061 0.2621 0.4636 200 0.1935 0.3145 400 0.0826 0.1895 600 0.0408 0.0605 200 0.1915 0.2580 400 0.0625 0.1613 600 0.0403 0.0504 200 0.0615 0.1126 400 0.0346 0.0406	6: Variation of total acid number (mg KOH/g) without ble ILs Conc. Time intervals (hrs.) 24 48 72 oil 0.061 0.2621 0.4636 0.7056 200 0.1935 0.3145 0.3752 400 0.0826 0.1895 0.2670 600 0.0408 0.0605 0.0934 200 0.1915 0.2580 0.3225 400 0.0625 0.1613 0.2419 600 0.0403 0.0504 0.0835 200 0.0615 0.1126 0.1895 400 0.0346 0.0406 0.0797 600 0.0302 0.0346 0.0635	6: Variation of total acid number (mg KOH/g) without and ble ILs Conc. ppm 24 48 72 96 oil 0.061 0.2621 0.4636 0.7056 0 200 0.1935 0.3145 0.3752 0 400 0.0826 0.1895 0.2670 0 600 0.0408 0.0605 0.0934 0 400 0.0625 0.1613 0.2419 0 600 0.0403 0.0504 0.0835 0 400 0.0615 0.1126 0.1895 0 600 0.0302 0.0346 0.0406 0.0797 0	6: Variation of total acid number (mg KOH/g) without and with ble ILs Conc. Time intervals (hrs.) 24 48 72 96 oil 0.061 0.2621 0.4636 0.7056 0.9130 k (without additive) 0.061 0.2621 0.4636 0.7056 0.9130 200 0.1935 0.3145 0.3752 0.4032 400 0.0826 0.1895 0.2670 0.3545 600 0.0408 0.0605 0.0934 0.1747 200 0.1915 0.2580 0.3225 0.3896 400 0.0625 0.1613 0.2419 0.3230 600 0.0403 0.0504 0.0835 0.1512 200 0.0615 0.1126 0.1895 0.2923 400 0.0346 0.0406 0.0797 0.1613 600 0.0302 0.0346 0.0635 0.0775 </td

Conversely, ΔG°_{ads} can be calculated by the relation $\Delta G^{\circ}_{ads} = \Delta G^{\circ}_{mic} - (0.6x \ \pi_{CMC} \ x \ A_{min})$

Table 5 shows some increase in ΔG° ads, supporting the idea of micellization over adsorption on the solution surface to overcome the repulsion forces occurring at the water/hydrophobe interface. ΔG°_{ads} and ΔG°_{mic} were always negative in value due to the spontaneity, and indicating that the processes are thermodynamically favored [50, 51].

3.3. Effect of IL₁₀₁₋₁₀₃ as base oil improvers:

We studied the effect of these prepared compounds as base oil improvers via:

3.3.1. Improvement in Total Acid Number values (TAN):

Total acid number is used as a guide in the quality control of lubricating oil. It is also used as a measure of lubricant degradation in service [52]. Figure 2 illustrated the behavior of blank sample against the oxidation process (from zero time up to 96 h, at 120 °C). It is obvious that, the rate of oxidation is increased with time. This result is attributed to that, oil is possibly being contaminated with acidic constituents, increasing the acid content in the oil, Scheme 1.

The maximum total acid number value appeared after 96 h (table 5). We noticed that, after adding compounds (IL₁₀₁₋₁₀₃) with different concentrations, the values of total acid number decreased.

Egypt. J. Chem. 66, No. 5 (2023)

Table 6 and figures (3-5) revealed that after thermal oxidation of the base oil up to 96 hours, in presence of additives, (IL₁₀₁₋₁₀₃), the TAN values decreased with increasing additives concentrations which ranged from 0.1935 up to 0.4032 mg KOH/g (200 ppm), 0.0826 to

0.3545 mg KOH/g (400 ppm), and from 0.0408 to 0.1747 mg KOH/g (600 ppm) respectively, Figures (3-5). This means that, stability of the base oil is increased by adding the prepared compounds, where the efficiency is ranked as follows: IL103 > IL102 > IL101.

TAN **2: Variation of TAN values of blank sample with** mg KOH/g







Figures 3, 4 and 5: TAN (mg KOH/g) variation of the base oil with and without IL₁₀₁, IL_{102, and} IL₁₀₃ (respectively) of concentrations 200, 400, and 600 ppm



and sludge, Table 7. The blank sample gave high reading (15.70 mm2/s) in viscosity after oxidation for 96 h. The viscosity values showed good results after adding the prepared compounds with different concentrations, table 7 and figures (6-8). These results illustrated that; the oxidation stability is improved in presence of the prepared additives.

3.3.3. Effect of IL101-103 on foaming characteristics

Foaming is a common problem with oil-lubricated components. Foam is a collection of small bubbles of air that accumulate on or near the surface of the fluid. The presence of air bubbles in the fluid can lead to excessive oxidation, cavitation, the reduction of

characteristics where the obtained foaming volume is considered high (170 ml) with long time (480 s) for foaming collapse, table 8. As shown in Table 8 and figures 9a-11b, the foaming characteristics of the base, after adding the prepared compounds with different concentrations were reduced compared to the blank sample, (from 480 up to 65 ml). Also, the foaming collapse time was reduced from 480.03 to 120.15 s. The efficiency of the additives as antifoams is ranked as follows: IL₁₀₃ > IL₁₀₂ >IL₁₀₁.

Figures 6, 7 and 8: Viscosity (mm^2/s) variation of the base oil with and without IL₁₀₁, IL_{102, and} IL₁₀₃ (respectively) of concentration: 200, 400, and 600 ppm



<u> </u>	ILs Conc.	Time intervals (h	rs.)		
Sample	ppm	24	48	72	96
Base oil Blank (without additive)	0	15.60	15.62	15.66	15.70
	200	15.46	15.51	15.60	15.63
IL101	400	15.42	15.47	15.54	15.57
	600	15.40	15.45	15.51	15.55
	200	15.49	15.53	15.56	15.59
IL102	400	15.48	15.50	15.53	15.57
	600	15.46	15.49	15.51	15.55
	200	15.56	15.58	15.60	15.61
IL ₁₀₃	400	15.55	15.57	15.59	15.60
	600	15.52	15.55	15.58	15.59

Table 7: Variation of viscosity at 100° C (mm2/s) with and without IL101-103

Figures 9, 10, and 11(a): Foaming volume (ml) variation of the base oil with and without IL₁₀₁, IL_{102, and} IL₁₀₃ (respectively) of concentrations 200, 400, and 600 ppm



Figures 9, 10, and 11 (b): Foaming collapse time (s) variation of the base oil with and without IL₁₀₁, IL_{102, and} IL₁₀₃ (respectively) of concentrations 200, 400, and 600 ppm



Sample	ILs Conc. ppm	Foaming Volume (ml)	Foaming Collapse Time (s)
Base oil Blank (without additive)	0	170	480.03
	200	120	225.23
IL101	400	110	204.09
	600	95	174.89
	200	105	197.39
IL102	400	90	169.55
	600	80	153.45
	200	95	176.92
IL ₁₀₃	400	80	149.29
	600	65	120.15

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

4. Conclusions

* The physicochemical characteristics of the delivered base oil is described.

* The structures of the prepared three compounds $(IL_{101-103})$ were well elucidated.

* Their surface parameters indicated that, they have good surface activity.

* They were tested as antioxidants and antifoams for local base oil, and the efficiency of them is ranked as follows: $IL_{103} > IL_{102} > IL_{101}$.

Conflicts of interest

There are no conflicts to declare.

References

- [1] Anthony E. Somers, Bhawna Khemchandani, Patrick C. Howlett, Jiazeng Sun, Douglas R. MacFarlane, and Maria 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 2013, 5, 11544–11553.
- [2] L. R. Rudnick; "Lubricant Additives: Chemistry and Applications", Second Edition, Taylor & Francis, 2009.
- [3] S. P. Srivastava; "Developments in Lubricant Technology", Wiley, 2014.
- [4] J. H. B. P. Ferreira and P. J. S.; "Voltametric determination of Zinc in lubricating Oils", Barbeira, Energ Fuel, 2009, 23, 3048-3053.
- [5] A. Adhvaryu, B. K. Sharma, H. S. Hwang, S. Z. Erhan and J. M. Perez; "Development of biobased synthetic fluids: Application of molecular modeling to structure-physical property relationship", Ind Eng Chem Res, 2006, 45, 928-933.
- [6] S. Z. Erhan, B. K. Sharma, Z. S. Liu and A. Adhvaryu; "Lubricant base stock potential of

chemically modified vegetable oils", J Agr Food Chem, 2008, 56, 8919-8925.

- [7] B. K. Sharma, J. M. Perez and S. Z. Erhan; "Soibean oil-based lubricants: a search for synergistic antioxidants", Energ Fuel, 2007, 21, 2408-2414.
- [8] F. Zhou, Y. Liang and W. Liu; "Ionic liquid lubricants: designed chemistry for engineering applications", Chemical Society reviews, 2009, 38, 2590-2599.
- [9] M. D. Bermudez, A. E. Jimenez, J. Sanes and F. J. Carrion; "Ionic Liquids as Advanced Lubricant Fluids", Molecules, 2009, 14, 2888-2908.
- [10] I. Minami; "Ionic Liquids in Tribology", Molecules, 2009, 14, 2286-2305.
- [11] S. Q. A. Rizvi; "A Comprehensive Review of Lubricant Chemistry, Technology, Selection, and Design", ASTM International, 2009.
- [12] Johnson, M.; Korcek, S. and Zinbo, M. "Inhibition of Oxidation by ZDTP and Ashless Antioxidants in the Presence of Hydroperoxides at 160 oC: Part I" SAE Technical Paper al (1986).
- [13] Klaus E.E., Ugwuzor D.I., Naidu S.K. and Duda J.L.; "Lubricant-Metal Interaction Under Conditions Simulating Automotive Bearing Lubrication", Proc. JSLE International Tribology Conf., 8-10, (1987), Tokyo, Japan, Elsevier, pp. 859-864.
- [14] George Koshy, Bilal Abdul Samad, Abhinand Suresh, Mohammed Shameem, Anil Payyappalli Mana; "Tribological Behavior of Phosphonium Based Ionic Liquid Blended with ZDDP", J. Européen des Systèmes Automatisés, Vol. 52, (2019), pp. 283-288.
- [15] Nikolai D. Denkov; "Mechanisms of Foam Destruction by Oil-Based Antifoams", Langmuir 2004, 20, 9463-9505.

- [16] Wang J, Wang M, Yang X, Zou W, Chen X; "Crystal structure and thermal decomposition kinetics of 1-(pyridinium-1-yl) propane-(1methylpiperidinium)bi[bis(trifuoromethanesulfon yl) imide], [PyC3Pi] [NTf2]2". Chin J Chem Eng 23, (2015), 816–821.
- [17] Damian K. Kaczmarek, Kamil Czerniak, Tomasz Klejdysz.; "Dicationic ionic liquids as new feeding deterrents", Chemical Papers (2018) 72:2457–2466.
- [18] Sharon I. Lall-Ramnarine, Sophia N. Suarez, Eddie D. Fernandez, Chanele Rodriguez, Sujun Wei, Mallory Gobet, J. R. P. Jayakody, Surajdevprakash B. Dhiman, and James F. Wishart. "Exploring the Use of Ionic Liquid Mixtures to Enhance the Performance of Dicationic Ionic Liquids", Journal of The Electrochemical Society, 164 (8) H5150-H5159 (2017).
- [19] Yi-Xin Sun, Ying-Ying Wang, Bing-Bing Shen, Bi-Xian Zhang and Xiao-Mei Hu; "Synthesis and investigation of physico-chemical properties of dicationic ionic liquids", R. Soc. open sci. 5, (2018), 181230.
- [20] Kralchevsky, P. A.; Nagayama, K.; "Particles at Fluid Interfaces and Membranes"; Elsevier: Amsterdam, 2001; Chapter 14.
- [21] Gwidon W. Stachowiak and Andrew W. Batchelor; "Engineering Tribology", Copyright © 2014 Elsevier Inc. ISBN: 978-0-12-397047-3.
- [22] Advaryu, A.; Sharma, Y.K.L and Singh, I.D.; "Studies on The Oxidative Behaviour Of Base Oils And Their Chromatographic Fractions", Fuel, 78, 1293-1302 (1999).
- [23] L. R. Rudnick; "Lubricant Additives: Chemistry and Applications", Second Edition, Taylor & Francis, (2009).
- [24] Z. Pawlak; "Tribochemistry of Lubricating Oils", Elsevier Science, 2003.
- [25] J. Qu, D. G. Bansal, B. Yu, J. Y. Howe, H. M. Luo, S. Dai, H. Q. Li, P. J. Blau, B. G. Bunting,
- G. Mordukhovich and D. J. Smolenski; "Antiwear performance and mechanism of an Oil-Miscible Ionic Liquid as lubricant additive" Acs Appl Mater Inter, (2012), 4, 997-1002.
- [26] Nessim, M. I., Ahmed, M. H. M., Ali A. M., Bassoussi, Salem, A. A. and Attia, S. K.; "The effect of some benzothiazole derivatives as antioxidants for base stock", International Journal of Current Research Vol. 5, Issue, 05, pp.1111-1117, (2013).
- [27] Hoda A. Mohammed, Maher I. Nessim, Ali A. M. El-Bassoussi, Doaa I. Osman and Magdy K. Zahran; "Novel Heterocyclic Compounds as Antioxidants for Egyptian Base Stock", Life Science Journal, (2014), 11, (9).
- [28] Maher I. Nessim, Doaa I. Osman, EL-Sayed K. Attia, Ebtsam A. Ahmed and Hoda A. Mohamed;

The role of 5-(4-alkoxybenzylidine)-2-thioxo-4oxo-1, 3-thiazolidine as antioxidants for Egyptian oil base stock", Int. J. Curr. Res. Chem. Pharma Sci. 2(2): (2015):80–93.

- [29] Maher I. Nessim, A.A. El-Bassoussi, M.Y. El-Kady, N. Hassan and Sameh M. Bidak; "Synthesis and evaluation of some thiazolidinones derivatives as antioxidants for local base stock", Advances in Environmental Biology, 10(12), (2016), 189-197.
- [30] J.S. Basta, A.A. El-Bassoussi, A.A. Salem, M.I. Nessim, M.H. Ahmed, S.K. Attia; "Preparation and evaluation of some benzimidazole derivatives as antioxidants for local base oil", Egyptian Journal of Petroleum, (2017) 26, 933–941.
- [31] S.A. Rizk, S.K. Attia, Doaa I. Osman and M.I. Nessim; "Synthesis and Applications of Pyridazinones for Base Oil Improvement", Egypt. J. Chem. 60, No. 1, pp. 129- 146 (2017).
- [32] Hoda A. Mohammed, Sayed K. Attia, Maher I. Nessim, Mohamed E. Shaaban and Ali A. M. El-Bassoussi; "Studies on Some Thiazolidinones as Antioxidants for Local Base Oil", Egypt. J. Chem. Vol. 62, No. 7, pp. 1219 - 1234 (2019).
- [33] Nessim, M. I., Bassoussi, A. A., Osman, D. I., Khalil H. F. and Ashmawy A. M.; "Preparation and evaluation of some azo-phenol derivatives as antioxidants for Egyptian base stock", Int. J. Curr. Res., Vol. 6, Issue, 10, pp.9203-9216, 2014.
- [34] A. M. Ashmawy, M. I. Nessim, E. M. Elnagar & D. I. Osman; "Preparation and evaluation of some novel liquid crystals as antioxidants", Mol. Cryst. & Liq. Cryst., 2017, Vol. 643, 188-198.
- [35] Ashraf M. Ashmawy, Sayed K. Attia, Maher I. Nessim, El-Sayed M. Elnaggar & Ali A. El-Bassoussi "Study on some azo liquid crystals as antioxidants for local base oil", Mol. Cryst. & Liq. Cryst., 2018, Vol. 668, No. 1, 78-90.
- [36] Ashraf M Ashmawy, Maher I Nessim, Doaa I Osman, El Sayed M Elnaggar, "Preparation and evaluation of some newly liquid crystal as antioxidant for base stocks", Iranian Chem. Commun., 7 (2019) 196-205.
- [37] M. M. Barakat, M. A. Deyab, M. I. Nessim, S. S. Abd El-Rehim, 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. 329, (2021), 115442.
- [38] Jui-Cheng Chang, Wen-Yueh Ho, I-Wen Sun, Yung-Liang Tung, Meng-Chin Tsui, Tzi-Yi Wu, Shih-Shin Liang; "Synthesis and characterization of dicationic ionic liquids that contain both hydrophilic and hydrophobic anions", Tetrahedron, 66, (2010), 6155.
- [39] M.I. Nessim, M.T. Zaky, M.A. Deyab: "Three new gemini ionic liquids: Synthesis, characterizations and anticorrosion applications", J. Mol. Liq. 266 (2018) 703–710.

- [40] FI El-Dib, SM Ahmed, Dina A Ismail, DE Mohamed. "Synthesis and Surface Properties of Novel N-Alkyl Quinoline-Based Cationic Gemini Surfactants." Journal of Dispersion Science and Technology 34 (4), 596-603 (2013).
- [41] Maher I. Nessim, Magda M. Osman & Dina A. Ismail. Surface-active properties of new cationic gemini surfactants with cyclic spacer. Journal of Dispersion Science and Technology, 39 (7), 1047-1055, (2018).
- [42] Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration, ASTM D664-18e2.
- [43] Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity, ASTM D445-21e1.
- [44] Standard Test Method for Foaming Characteristics of Lubricating Oils (ASTM D892 - 18).
- [45] S.D. Wettig, R.E. Verrall,; "Thermodynamic Studies of Aqueous m-s-m Gemini Surfactant Systems", J. Colloid Interface Sci. 235 (2001) 310.
- [46] R. Zana,; "Dimeric (Gemini) Surfactants: Effect of the Spacer Group on the Association Behavior in Aqueous Solution", J. Colloid Interface Sci. 97 (2002) 203.
- [47] L. Grosmaire, M. Chorro, C. Chorro, S. Partyka, R. Zana,; "Alkanediyl-α,ω-Bis (dimethyl alkylammonium Bromide) Surfactants: 9. Effect of the Spacer Carbon Number and Temperature on the Enthalpy of Micellization", J. Colloid Interface Sci. 246 (2002).
- [48] Nakahara, H., Nishino, A., Tanaka, A., Fujita, Y., Shibata, O., Interfacial behavior of gemini surfactants with different spacer lengths in aqueous medium. Colloid Polym. Sci. (2019) 297, 183–189.
- [49] Nakahara, H.; Nishino, A.; Tanaka, A.; Fujita, Y.; Shibata, O., "Interfacial behavior of gemini surfactants with different spacer lengths in aqueous medium", Colloid Polym. Sci. (2019), 297, 183–189.
- [50] Sahar M. Ahmed, Taisir. T. Khidr & Dina A. Ismail, "Effect of gemini surfactant additives on pour point depressant of crude oil", Journal of Dispersion Science and Technology, 39, 8, 1160-1164 (2018).
- [51] C.E. El shafiee, R.A. El-Nagar, M.I. Nessim, M.M.H. Khalil, M.E. Shaban, Rima D. Alharthy, D.A Ismail, R.I. Abdallah, Y.M. Moustafa, "Application of asymmetric dicationic ionic liquids for oil spill remediation in sea water", Arabian Journal of Chemistry. (2021) 14, 103123. [52] A.Y. El-Naggar, R. A. El-Adly, T. A.

Altalhi, A. Alhadhrami, F. Modather, M. A.

Egypt. J. Chem. 66, No. 5 (2023)

Ebiad & A. Salem; "Oxidation stability of lubricating base oils", Petroleum Science and Technology, 36, 3, 179-185, (2018).