Preparation and Tribological Properties of New Bisimidazolium Ionic Liquids

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Abstract— In this paper two new bisimidazolium based ionic liquids (ILs), 3,3'- (3,6,9,12,15- pentaoxaheptadecane-1,17-diyl) bis(1-vinyl-1H-imidazol-3-ium) methanesulfinate (1a), 3,3'- (3, 6,9,13-tetraoxapentadecane-1,15-diyl)bis(1-vinyl-1H-imidazol-3-i um)methanesulfinate (1b) were prepared. Their structures were characterized with ^{1}H and ^{13}C NMR, and Mass Spectroscopy. Tribological behavior of 1a and 1b ILs was studied.

Index Terms— Bisimidazolim ionic liquids, NMR, Mass, Four ball tester, Friction and Wear

1.INTRODUCTION

In recent years, ILs have started to play vital role in additives of lubricants for their potential in emission reduction and improving fuel economy. Room temperature ILs are designated as salts having their melting points lesser than the atmospheric temperature. These are synthesized by mutation of an organic particle cation and another organic particle anion. ILs has preferred consideration attention as neat lubricants along with additive of lubricants [1-8].

Imidazolium based ILs were globally experimented additives for lubricants. The accumulation of 1% by wt of imidazolium ILs signification increased the anti-wear status of base oil or fats there by reducing its friction aggressively [9-13].

ILs were also castoff as base oil, with the economical point view the ILs as neat lubricant is not feasible, because of their price. Therefore they would be preferably used as additives in the lubricate industry.

Benzotriazole ILs used as the additives for liquid lubricants showed prominent tribologcal behavior [15,16]. G Hang etal, reported anti wear behavior of Guanidium ILs at high temperature [17]. Bisimidazolium ILs shown high performance anti wear property [18].

In this view, we prepared two vinyl substituted Bisimidazolium ILs, in a simple process. The structures were characterized and studied tribology properties in this paper.

2. EXPERIMENTAL DETAILS:

2.1. CHEMICAL

All the chemicals procured from Sigma Aldrich in purified form. Fig. (1) elucidates the chemical bonding of ILs, 3,3'-(3,6,9,12,15-pentaoxaheptadecane-1,17-diyl) (1-vinyl-1H-imidazol-3-ium) methanesulfinate (1a) and 3,3'-(3,6,9,13-tetraoxapentadecane-1,15-diyl) (1-vinyl-1H-imidazol-3-ium) methanesulfinate (1b), which were synthesized from 1-Vinyl-1H-imidazole (1) when reacted with hexaethylene glycol dimesylate (a) and pentaethylene glycol dimesylate (b) in the presence Acetonitrile solvent at 90 0C about 24 hr to form ILs 1a and 1b respectively.

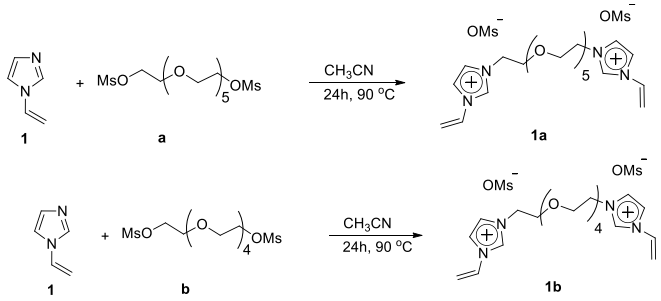

Figure 1: Preparation of 3,3'- (3,6,9,12,15-pentaoxaheptadecane-1, 17-diyl) (1-vinyl- 1H-2-imidazol-3-ium) methanesulfinate (1a) 3,3 '-(3,6, 9,13-tetraox apentadecane-1,15-diyl) (1-vinyl-1H-2-imidazol- 3-ium) methanesulfinate (1b)

Preparation of 3,3'- (3,6,9,12,15- pentaoxaheptadecane -1,17-diyl)(1-vinyl-1H-2-imidazol-3-ium) methanesulfinate (1a)

Every drop of 1-Vinyl-1*H*-imidazole (1.88 g, 20 mmol) (**1**) was supplemented to the solution of 4.38 g (10.00 mmol) of hexaethylene glycol dimesylatein (**a**) dry CH_3CN (100 mL). The reaction mixture was agitated for 48 hours of standard time at 90^0C. At this point, the rotary and revolutionary evaporation takes place and furthermore this solvent mix was splashed with100 ml ethyl acetate which was then dehydrated overnight at atmospheric conditions. (**1a**), 5.25 g (83.8 %) as a pale yellow solid.^{1}H-NMR (400 MHz, DMSO-D_6) δ δ 9.45 (t; J : 1.3 Hz, 2H), 8.20 (t; J : 1.8 Hz, 2H), 7.88 (t; J : 1.6 Hz, 2H), 7.32 (q; J : 8.2 Hz, 2H), 5.99 (d; J : 2.3 Hz, 2H), 5.95 (d; J : 2.3 Hz, 2H), 5.43 (dd; J : 8.7, 2.3 Hz, 2H), 4.38 (d; J : 5.0 Hz, 4H), 3.79 (t; J : 4.8 Hz, 4H), 3.56-3.44 (m, 14H), 2.31 (s, 6H); 135.7, 128.6, 123.5, 118.6, 108.8, 69.4, 68.3, 67.8, 66.5, 50.3 49.5, 39.3. $C_{24}H_{42}N_4O_{11}S_2$ ($M+H^+$) 626.7463, 626.7460.

Preparation of 3,3'-

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(3,6,9,13 -tetraoxapentadecane -1,15-diyl)bis(1-vinyl-1H-imidazol-3-ium) methanesulfinate (1b)

1-Vinyl-1*H*-imidazole (1.88 g, 20 mmol) (**1**) was added as continuous drops of similar size to the solvent of 3.94 g (10.00 m/mol) of pentaethylene glycol dimesylatein (**b**) dry CH_3CN (100 mL). The reaction mix solvent was agitated at 90 °C for 2 consecutive days . At this instance, the reaction solvent mix was concerted by rotary agitated evaporation; and was washed several times with ethyl acetate (100 mL) and dehydrated under high vacuum overnight at atmospheric temperature to afford (**1b**) 5.15 g (88 %) as a light yellow solid.^{1}H-NMR (400 MHz, DMSO-D_6) δ δ 9.46 (t; J : 1.2 Hz, 2H), 8.23 (t; J : 1.7 Hz, 2H), 7.86 (t; J : 1.5 Hz, 2H), 7.34 (q; J : 8.4 Hz, 2H), 5.96 (d; J : 2.4 Hz, 2H), 5.93 (d; J : 2.4 Hz, 2H), 5.47 (dd; J : 8.5, 2.5 Hz, 2H), 4.40 (d; J : 6.0 Hz, 4H), 3.81 (t; J : 4.6 Hz, 4H), 3.55-3.43 (m, 10H), 2.33 (s, 6H); ^{13}C NMR (100. MHz, DMSO-d_6) δ: 134.8, 129.3, 123.9, 119.9, 108.5, 69.9, 66.7, 49.3, 45.4, 39.3. HRMS (ESI, m/z): calcd for $C_{22}H_{38}N_4O_{10}S_2$ ($M+H^+$) 582.6912, found: 582.6908.

2.2 CHARACTERIZATION:

Polyethylene glycol (PEG) procured from Sigma Aldrich possess an average molecular weight of about 190 to 200 g/mol. The two ILs 1a and 1b significantly miscible with PEG can be used as additives, presented in Table 1.

The miscibility of 1a and 1b ILs

	1a IL	**1b** IL
Miscibility (Weight fraction)	3-5 %	3-6 %

Table 1

The density and viscosity allied properties were measured by Kinematic Viscometer, Stanhope-Seta, presented in Table 2.The thermal statics of the P.E.G with ILs were stated with Perkin Elmer thermo analyzer.

Properties and characteristic features of PEG and ILs as condiments

Lubricants	Kinetic Viscosity in mm^2/s		Viscosity Indices	Density Kg/m^3 at 25.0 ^{0}C
	40.0^{0}C	100.0 ^{0}C		
P.E.G	22.62	4.21	78.7	1127.5
PEG + 0.5 % **1a**IL	22.86	4.24	78.9	1128.6
PEG + 1.0 % **1a**IL	23.44	4.31	82.1	1129.6
PEG + 2.0 % **1a**IL	24.78	4.40	83.9	1130.7
PEG + 0.5 % **1b**IL	22.87	4.31	79.3	1128.8
PEG + 1.0 % **1b**IL	23.59	4.33	84.4	1129.4
PEG + 2.0 % **1b**IL	24.79	4.42	85.3	1132.7

Table 2

2.3 TRIBOLOGY TEST:

The tribology test outcomes done on the PEG with additives were evaluated using steel &steel contact surfaces with four ball testers at 1000C correspondingly, with ball disc configuration. By frequently persuading the upper ball in running condition of ϕ 10mm in diameter, AISI 52100 steel, hardness of 59-61 HRC against the lower stationary diskette of ϕ24 mm x 7.9mm, for 30 min duration.

The four-ball test was also conducted by equivocating an AISI 52100 steel ball. As an outcome of the above test the wear scar diameter (WSD) on the three lower balls and the coefficient of friction were set-down automatically.

3. RESULT AND DISCUSSIONS:

3.1 Characteristic properties of the manufactured ILs: The mixture of ILs to P.E.G increases its viscidness in a meager manner which implies that the increase in viscosity is concentration dependent. (Table 2).

The thermoravimetric analysis (figure 2) illustrates that the ILs do not unveil any weight loss between the temperature of 2000Cand below 6000C thereby indicating a very high thermal stability .

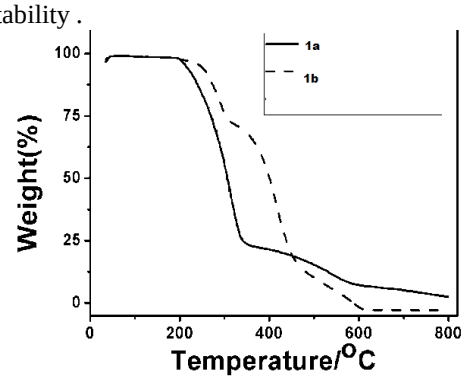

Figure:2 TGA curve of 1a and 1b in air

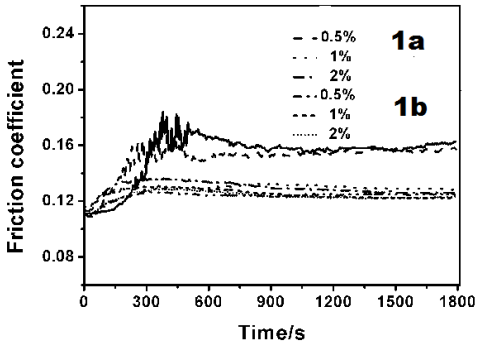

Figure:3 Progression of coefficient of friction

3.2 Friction and wear Behavior:

Effect of Additive Concentration: Figure 3 exhibits the evaluation of the corresponding coefficient of friction at a load condition of 100N for with 1a different additive concentrations changed gradually and the wear status of the discs made of steel after the changes incorporated at each stage after testing. The outcomes are elucidated below:

4. CONCLUSION

Two Bisimdazolium ionic liquids (ILs) as mentioned previously named as , 3,3'- (3,6,9,12,15-pentaoxaheptadecane-1,17-diyl)(1-vinyl-1H-imidazol-3-ium) methanesulfinate (1a), 3,3'-(3,6,9,13 -tetraoxapentadecane-1,15-diyl)(1-vinyl-1H-imidazol-3-ium) methanesulfinate (1b) were prepared and characterized. Their tribology properties were studied using Pin-on-disc tribometer and four ball tester.

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