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Pyridinium based dicationic ionic liquids as base lubricants or lubricant additives

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ABSTRACT

A series of eight new dicationic ionic liquids incorporating polyethylene glycol chains linking two *N*-alkylpyridinium moieties through rings position 2, were synthesized and investigated for their potential use as lubricants or lubricant additives. Alkylsulfate and bis(trifluoromethanesulfonyl)imide [NTf_2] were selected as anions. Dicationic ionic liquids containing [NTf_2] anion demonstrated good properties as neat lubricants showing low coefficient of friction and wear comparable with the reference lubricant (glycerol). Even more interesting could be their use as friction modifier additives since an important decrease in the coefficient of friction was achieved with a really low concentration of ionic liquid. The thermal analysis of all ionic liquids by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) is also described.

1. Introduction

Ionic liquids (ILs) have gained increasing importance both in the scientific and industrial engineering community during last decade. Due to their remarkable and interesting properties, such as negligible vapor pressure, non-flammability, high polarity, and high thermal stability [1]. ILs are finding widespread use as engineering fluids or as novel lubricating systems [2,3]. Moreover, the polar nature of ILs is directly connected with good tribological behavior, since their strong interactions with surfaces lead to the formation of adsorbed films, reducing friction and wear.

The first experiment of ILs in tribology was reported in 2001 with the work of Liu et al. [4]. In that research, imidazolium tetrafluoroborate was tested as IL-based lubricant for various tribo-pairs and, in all experiments, the use of the IL showed significant friction reduction. Since that time, the interest of scientists in tribological properties of ILs has considerably increased [5,6]. Jones et al. have shown that the presence of polyether chains can significantly improve tribological behavior of liquid lubricants or lubricant additives [7]. Jin et al. have examined some polyethylene glycol functionalized ILs as high temperature lubricants, showing how the presence of fluorine in the IL favorably boosts its anti-wear performance [8]. On the other side, dicationic ILs based on imidazolium and pyrrolidinium cation and traditional anions as BF_4^- or PF_6^-, have shown good thermal stability comparing with their monocationic analogues [9]. It has also been shown that that the acute toxicity of DILs is in many cases below the levels observed for those monocationic and that the use of head groups connected via polyethylene glycol could be identified as structural elements reducing the toxicity [10]. Hence, the combination of the tribologically favorable properties of polyethylene glycol and DILs may lead to a series of novel and advanced lubricating systems.

Previous works on the use of DILs derived from imidazolium [11,12] and pyrrolidinium [13] for lubrication have shown very promising results. Nevertheless, to our knowledge, no papers were published about using pyridinium DILs as lubricants or lubricant additives. It is known that pyridinium cation can show exceptionally high levels of biodegradation under aerobic conditions and can be classified as “ready biodegradable” [14]. In addition, studies on the acute toxicity of DILs have shown levels below those observed for monocationic ILs [15]. Several recent studies dealing with tribological properties of ionic liquids exposed to extreme conditions [16,17], as well as with the stability of lubricant mixtures of ionic liquids with conventional base oils [18], has been published. Generated knowledge of ionic liquids in tribology can also be found in several review articles [2,19].

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For all these reasons, we have synthesized and studied the tribological properties of a series of DILs that incorporate polyethylene glycol chains linking two alkylpyridinium moieties. Alkylsulfate [RSO_4] and bis(trifluoromethane) sulfonimide [NTf_2] were selected as anions taking into account the reduction on wear and friction observed when these anions were used in previous works on monocationic ILs [20,21].

2. Experimental

2.1. Materials and measurements

Hexaethylene glycol (≥ 97.0%) was purchased from Sigma Aldrich (Steinheim, Germany). Pyridine (≥ 99.0%), thionyl chloride (≥ 99.7%), 2-picoline (≥ 98.0%), tetraethylene glycol (≥ 99.0%) and *n*-butyllithium (2.5 M solution in hexane) were received from Acros Organics (Madrid, Spain). Dimethyl sulfate (≥ 99.0%), diethyl sulfate (≥ 99.0%) and 1,4-dioxane were purchased from Fluka (Steinheim, Germany). Dichloromethane (≥ 99.9%), ethyl acetate (≥ 99.5%), *n*-hexane (≥ 99,9%) and diethyl ether (≥ 99.9%) were obtained from Merck (Madrid, Spain). Solvents were dried with suitable drying agents ($CaCl_2$ for dichloromethane, K_2CO_3 for ethyl acetate, and CaH_2 for *n*-hexane and diethyl ether) and distiled under Ar. The analysis of NMR (400 MHz) of the obtained ILs confirmed impurity levels lower than 1% (mole fraction) in all cases.

Column chromatography was performed on Kieselgel 60 silica gel. Preparative thin layer chromatography (TLC) was carried out on 25 aluminium sheets (TLC silica gel 60 F_{254}) from Merck KGaA to follow the progress of the reactions. The chromatograms were developed in mixtures of methanol and dichloromethane or ethyl acetate and hexane in different proportions. Spots were visualized by UV light (254 nm) and developed using iodine (I_2).

The ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker ARX at 400.1621, 100.6314 and 376.5266 MHz respectively. $CDCl_3$ (Armar AG, 99.8%D), D_2O (Panreac, 99.8%D) and $(CD_3)_2CO$ (Panreac, 99.8%D) were used as solvents. Chemical shifts are given in parts per million and coupling constants (*J*) in hertz. MestReC (4.7.0.0) was used for data interpretation. Electrospray MS spectra were recorded on a Bruker FTMS apex-Qe spectrometer.

Differential scanning calorimetry (DSC) was used to measure thermal transitions of the ILs in a temperature range from 243 K to 433 K. The samples were measured in closed aluminum pans with a small hole in the lid using a Mettler-Toledo DSC, model DSC1, STAR^e System with automatic sample changer. The sample weight was between 15 mg and 20 mg and all experiments were performed under a nitrogen flow of 50 mL/min. In order to avoid the effect of the presence of volatiles in ILs, the samples were preheated at 393 K for 20 min inside the furnace of the DSC. The thermal treatment includes: heating the IL from 243 K to 433 K with a heating rate of 10 K/min and final cooling from 433 K to 243 K with a cooling rate of − 10 K/min.

The thermal stabilities of the ILs were measured using thermogravimetric analysis (TGA). 10–15 mg of the samples were measured in open platinum pans using a SDT Q600 (TA Instruments, USA) under nitrogen flow (50 mL/min). The measurements started at room temperature and were completed at 873 K with a heating rate of 10 K/min. TGA was utilized to measure the start of decomposition temperature, T_{start} and the onset of decomposition temperature, $T_{d,onset}$. The onset temperature ($T_{d,onset}$) was calculated by the intersection of the straight baseline along the temperature axis from a low temperature region where there is no weight loss, and a straight line created through the inflection point of the mass versus temperature data. The start temperature (T_{start}) was taken from the start of the inflection point [22].

2.2. Synthesis

2.2.1. General procedure for the synthesis of pyridinium functionalized polyethylene glycols **4**, **5** (procedure A)

A stirred solution of 2-picoline (**1**) (2 equiv.) in anhydrous THF (25 mL) was cooled to 273 K by an ice bath under Ar atmosphere. An ice-cold solution of *n*-BuLi 2.5 M in hexane (2 equiv.) was added dropwise and the reaction mixture was stirring for 3 h at 273 K. The corresponding chlorinated polyethylene glycol **2** or **3** (1 equiv.) in anhydrous hexane was then added dropwise and the reaction mixture was kept stirring at r.t for 17 h. The reaction mixture was then neutralized with a saturated solution of NH_4Cl and the solvent was removed on a rotary evaporator. The residue was dissolved in dichloromethane and washed twice with distill water. The organic extracts were combined, dried over with Na_2SO_4 and filtered. The solvent was removed on the rotary evaporator and the residue was purified by column chromatography (silica gel, $CHCl_3$/MeOH 10:1).

2.2.2. 1,13-Di(pyridine-2′-yl)-4,7,10-trioxatridecane (**4**)

Following the general procedure A, 2-picoline (**1**, 0.80 g, 8.64 mmol), *n*-BuLi 2.5 M in hexane (3.46 mL, 8.46 mmol) and dichlorotetraethylene glycol **2** (0.50 g, 2.16 mmol) in anhydrous hexane (10 mL) were reacted in THF (25 mL). Yield 82% (M_n=344.45 g/mol). ^1H NMR ($CDCl_3$): δ 8.51 (2*H*, m), 7.52 (2*H*, td,, J_1=7.7 Hz, J_2=1.9 Hz), 7.11 (2*H*, d, *J*=7.8 Hz), 7.04 (2*H*, ddd, J_1=7.4 Hz, J_2=4.9 Hz, J_3=1.0 Hz), 3.62-3.53 (8*H*, m), 3.47 (4*H*, t, *J*=6.5 Hz), 2.82 (4*H*, t, *J*= 7.7 Hz), 1.99 (4*H*, m). ^{13}C NMR ($CDCl_3$): δ 29.5, 34.8, 70.1, 70.5, 70.6, 121.0, 122.9, 136.3, 149.2, 161.7. Electrospray MS *m/z* (%) 367.1992 $[M+Na]^+$ ($C_{20}H_{28}N_2NaO_3$ requires 367.1998, 16), 345.21726 $[M+H]^+$ ($C_{20}H_{29}N_2O_3$ requires 345.2178, 100).

2.2.3. 1,19-Di(pyridin-2′-yl)-4,7,10,13,16-pentaoxanonadecane (**5**)

Following the general procedure A, 2-picoline (**1**, 1.94 g, 20.9 mmol), *n*-BuLi 2.5 M in hexane (8.4 mL, 20.9 mmol) and dichlorohexaethylene glycol (**3**, 2.67 g, 8.4 mmol) were treated in THF (60 mL). Yield 82% (M_n=344.45 g/mol). ^1H NMR ($CDCl_3$): δ 8.50 (2H, m), 7.57 (2*H*, td, J_1=7.7, Hz, J_2= 1.9 Hz), 7.15 (2*H*, d, *J*=7.8 Hz), 7.08 (2*H*, ddd, J_1=7.4 Hz, J_2=4.8 Hz, J_3=1.1 Hz), 3.65-3.55 (16*H*, m), 3.49 (4*H*, t, *J*=6.5 Hz), 2.85 (4*H*, t, *J*=7.7 Hz), 2.01 (4*H*, *m*). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ ppm): 161.7, 149.2, 136.2, 122.9, 121.0, 70.6, 70.5, 70.1, 34.8, 29.5. Electrospay MS *m/z* (%) 433.2697 $[M+H^+]$ ($C_{24}H_{37}N_2O_5$ requires 433.2702, 100).

2.2.4. General procedure for the synthesis of pyridinium alkylsulfate (**6**–**9**) (procedure B)

A stirred solution of the pyridine—functionalized polyethylene glycol **4**–**5** (1 equiv.) in dry MeCN was cooled to 273 K under Ar atmosphere and the corresponding dialkylsulfate (2.1 equiv.) was added by small portions. The ice bath was removed and the reaction mixture was allowed to stir under reflux at 354 K until completion of the reaction as indicated by t.l.c. ($CHCl_3$–MeOH, 10:1). The reaction mixture was then cooled at r.t and the solvent was evaporated. The obtained residue was purified by washing with AcOEt and remaining solvent was removed by heating under reduced pressure. The desired DIL was dried by heating at 343.15 K and stirring under vacuum (2×10^{-1} Pa) for 48 h.

2.2.5. 1,13-Di(N-methylpyridinium-2′-yl)-4,7,10-trioxatridecane di (methylsulfate) (**6**)

Following procedure B, the pyridine functionalized [C_2py ($CH_2OCH_2)_3C_2$py] **4** (0.49 g, 1.42 mmol) and dimethyl sulfate (0.38 g, 2.99 mmol) were reacted in MeCN (10 mL) for 20 h. Yield 97% (M_n=596.71 g/mol). The percentage of water content was