IONIC LIQUIDS BASED ON BIS(TRIFLUOROMETHYLSULFONYL)IMIDE OR ALKYLSULFATE ANIONS AS NEAT LUBRICANTS IN STEEL-STEEL CONTACTS

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Introduction: Development of lubricants for gears is very complex and has important implications to economy and environment. In the last decade, ionic liquids (ILs) have been proposed to be used as base lubricants or lubricant additives in different studies [1-3] due to their unique properties. Their chemical structure determines largely the tribological performance, so this possibility of controlling the physicochemical properties of ILs by changing their ions is another advantage for the preparation of tailor-made lubricants for special applications [4]. The ILs most widely studied, those containing the anions $[BF_4]^-$ and $[PF_6]^-$, decompose in presence of water to produce corrosive hydrogen fluoride [1,3]. Alternative ILs have started to be studied, for example ILs with the anions bis(trifluormethylsulfonyl)imide, $[NTf_2]^-$, alkylsulfate, $[C_nSO_4]^-$, or tris(tetrafluoroethyl)trifluorophosphate, $[(C_2F_5)_3PF_3]^-$. Alkylsulfate anions are halogen-free and ILs like $[C_2C_1im][C_2SO_4]$ are being studied as lubricants for microelectromechanical systems (MEMS) among other applications[5]. Furthermore, the alkyl side length of $[C_2C_1im][C_nSO_4]$ modifies their sensitivity to hydrolysis, being lower for ILs with longer alkyl chain [6]. Thus, a higher hidrophobicity was reported as a good characteristic to obtain a better tribological behaviour [7]. $[NTf_2]^-$ and $[(C_2F_5)_3PF_3]^-$ are examples of hydrophobic anions [1] and ILs base on each of them have shown good results as lubricants. In this work we present the tribological behaviour of four ionic liquids (ILs), two of them containing an alkylsulfate anion (1-ethyl-3-methylimidazolium ethylsulfate, $[C_2C_1Im][C_2SO_4]$, and 1-ethyl-3-methylimidazolium hexylsulfate, $[C_2C_1Im][C_6SO_4]$) and the other two a bis(trifluoromethylsulfonyl)imide anion (1-(2-methoxyethyl)-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide, $[C_1OC_2C_1Pyrr][NTf_2]$, and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, $[C_4C_1Pyrr]$ $[NTf_2]$.

Experimental: Samples of the four ILs were kindly provided by Merck (Germany) with purity ≥98%. Before being used, they were treated under vacuum pressure (10 Pa) at room temperature, for at least 48 h, to remove by evaporation the residual volatile impurities. Tribological tests were carried out at room temperature, in air, under a normal load of 8 N with a sliding velocity of 0.02 m/s and for a sliding distance of 20 m, using a reciprocating ball-on-plate CSM Standard tribometer. The upper ball, made of AISI100Cr6 stainless steel (diameter of 0.5 mm, hardness 848 HV), slid against an AISI 420 (hardness 245HV) stainless steel prismatic plate with five drops of lubricant previously inserted in the contact area. The friction coefficient curve with the sliding distance was generated automatically by the tribometer software. Each test was repeated eight times and the average friction coefficient was provided. Volume loss of the lower plate due to wear was determined from cross-section area measurements of each wear track at five equidistant points using a DEKTAK^3 stylus profilometer.

Results and discussion: Figure 1 shows an example of the friction coefficient recorded as function of sliding time for the four ILs. In this figure can be seen that, at the end of the test, the friction coefficient is almost stable for all the ILs, but only for the $[C_2C_1Im][C_6SO_4]$ this value is lower than at the firsts 750 seconds. The worst result was obtained for $[C_1OC_2C_1Pyrr][NTf_2]$, which reached a value of approximately 0.06.

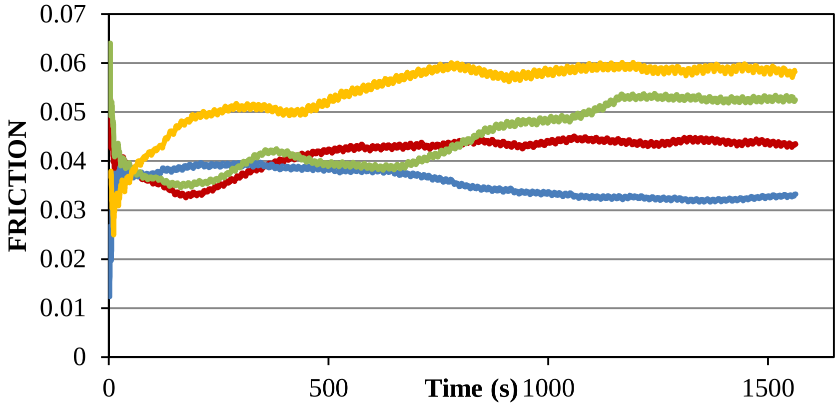

Figure 1. Sliding friction recording for the ILs studied: $[C_2C_1Im][C_2SO_4]$, $[C_2C_1Im][C_6SO_4]$, $[C_4C_1Pyrr][NTf_2]$, $[C_1OC_2C_1Pyrr][NTf_2]$.

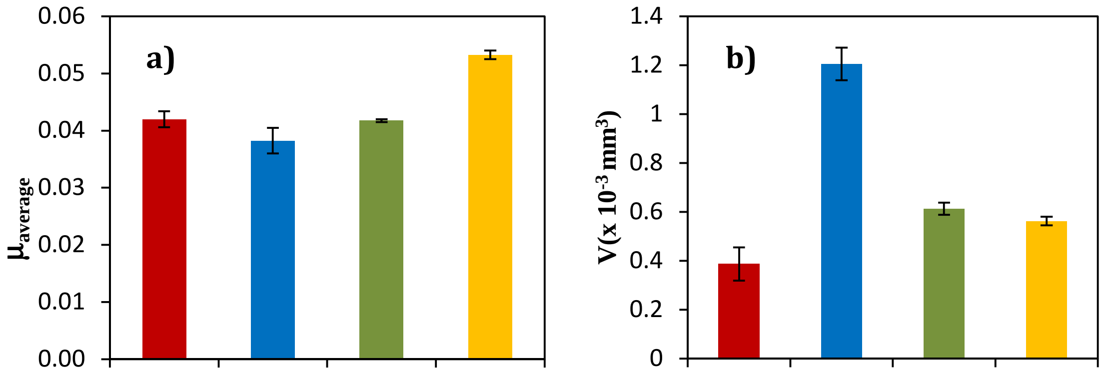

Figure 2. a) Mean friction coefficients, $\mu_{average}$, and b) wear volume loss, V, produced with the ILs studied: $[C_2C_1Im][C_2SO_4]$, $[C_2C_1Im][C_6SO_4]$, $[C_4C_1Pyrr][NTf_2]$, $[C_1OC_2C_1Pyrr][NTf_2]$. Error bars are also indicated.

Regarding the friction coefficient average, the results presented in Figure 2a show that the lowest value was obtained with $[C_2C_1Im][C_6SO_4]$ (0.038), followed by $[C_2C_1Im][C_2SO_4]$ and $[C_4C_1Pyrr][NTf_2]$ (0.042 in both cases) and, finally, the worst was $[C_1OC_2C_1Pyrr][NTf_2]$ (0.053).

Concerning the wear volume loss (Figure 2b) the order, from the lowest to the highest, was: $[C_2C_1Im][C_2SO_4] < [C_1OC_2C_1Pyrr][NTf_2] < [C_4C_1Pyrr][NTf_2] < [C_2C_1Im][C_6SO_4]$. So the IL with the lowest friction coefficient had the highest wear volume loss, and the one with the worst friction coefficient was the second better in wear volume loss. Similar results, where the IL was able to reduce the friction but not the wear loss, were obtained by Qu *et al.*[8] and were attributed to possible tribochemical reactions.

Conclusions: Four ILs, two containing alkylsulfate and two with bis(trifluoromethylsulfonyl)imide anions, were studied as neat lubricants. The tribological results showed that the $[C_2C_1Im][C_6SO_4]$ reached the lowest friction coefficient, but was not able to reduce the wear volume loss. Comparing the anions, at least one of the alkylsulfate ILs was better, in friction coefficient or wear volume loss, than both ILs with $[NTf_2]$.

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References:

1. F. Zhou, Y. Liang and W. Liu, Ionic liquid lubricants: designed chemistry for engineering applications, *Chemical Society Reviews* 38 (2009) 2590-2599.
2. A. Pensado, M. Comuñas and J. Fernández, The Pressure–Viscosity Coefficient of Several Ionic Liquids, *Tribology Letters* 31 (2008) 107-118.
3. M. Uerdingen, Ionic Liquids as Lubricants, in *Handbook of Green Chemistry*, Ed.,P. Wasserscheid and A. Stark, Chapter 8, pp. 203-219, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2010.
4. T. Torimoto, T. Tsuda, K. Okazaki and S. Kuwabata, New Frontiers in Materials Science Opened by Ionic Liquids, *Advanced Materials* 22 (2010) 1196-1221.
5. J.J. Nainaparampil, K.C. Eapen, J.H. Sanders and A.A. Voevodin, Ionic-Liquid Lubrication of Sliding MEMS Contacts: Comparison of AFM Liquid Cell and Device-Level Tests, *Journal of Microelectromechanical Systems* 16 (2007) 836-843.
6. P. Wasserscheid, R.v. Hal and A. Bosmann, 1-n-Butyl-3-methylimidazolium ([bmim]) octylsulfate-an even 'greener' ionic liquid, *Green Chemistry* 4 (2002) 400-404.
7. T. Itoh, N. Watanabe, K. Inada, A. Ishioka, S. Hayase, M. Kawatsura, I. Minami and S. Mori, Design of Alkyl Sulfate Ionic Liquids for Lubricant,. *Chemistry Letters* 38 (2009). 64-65.
8. J. Qu, J.J. Truhan, S. Dai, H. Luo and P.J. Blau., Ionic liquids with ammonium cations as lubricants or additives, *Tribology Letters* 22 (2006) 207-214.