IONIC LIQUIDS AS GEAR LUBRICANTS AND HYDRAULIC FLUIDS

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Introduction: The lubricants that are mainly used today are mineral oil-based, i.e. restricted in their chemical structures and properties. Synthetic lubricants can overcome some of the problems for higher temperature stability, higher loads with better tribological behaviour and reduced noise. Nevertheless, high thermal stability lubricants are needed in aircrafts, spacecrafts as well as a variety of industries, including chemical, textile, tire, conveyor, oil and gas, glass, plastic film, and non-woven manufacturing, mining and metal processing. Ionic liquids (ILs) are considered potential lubricants due to their inherent polarity, high thermal stability, negligible volatility and non-flammability as well as for the high flexibility of their molecular design. Besides, several ILs have low compressibilities which made them excellent hydraulic fluids. This new class of more effective, environmentally-friendly lubricants could lead to huge energy saving [1-4]. In our laboratory we have performed several studies to extend the existing work on ILs as lubricants for their application in elastohydrodynamic lubrication (bearings, rollings, gearboxes...) and as hydraulic oils among other applications. These studies consist in the measurements of the density and viscosity in broad ranges of temperature and pressure, of the thermal stability of several ILs, and of the tribological properties of several lubricated-surface contacts. We have also analyzed the structure influence on thermophysical and tribological properties, which will permit to create tailor-made lubricants and hydraulic fluids [4-7].

Experimental: Samples were kindly provided by Merck for ten ILs composed by the cations 1-ethyl-3-methylimidazolium, $[C_2C_1im]^+$, 1-butyl-2,3-dimethylimidazolium, $[C_4C_1C_1im]$, 1-butyl-1-methylpyrrolidinium, $[C_4C_1Pyrr]^+$, 1-(2-methoxyethyl)-1-methyl-pyrrolidinium, $[C_1OC_2C_1Pyrr]^+$ or trihexyl(tetradecyl)phosphonium $[P_{6,6,6,14}]^+$ and the anions ethylsulfate, $[C_2SO_4]^-$, hexylsulfate $[C_6SO_4]^-$, trifluoromethanesulfonate $[CF_3SO_3]^-$, bis(trifluoromethy-lsulfonyl)imide, $[NTf_2]^-$, or tris(pentafluoroethyl)trifluorophosphate, $[(C_2F_5)_3PF_3]^-$. The ILs are $[C_2C_1im][C_2SO_4]$, $[C_2C_1im][C_6SO_4]$, $[C_4C_1C_1im][NTf_2]$, $[C_4C_1C_1im][(C_2F_5)_3PF_3]$, $[C_4C_1Pyrr][CF_3SO_3]$, $[C_4C_1Pyrr][NTf_2]$,$[C_4C_1Pyrr][(C_2F_5)_3PF_3]$,,$[C_1OC_2C_1Pyrr][NTf_2]$, $[C_1OC_2C_1Pyrr]$ $[(C_2F_5)_3 PF_3]$, and $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$.

Apparatus. Densities and viscosities were measured for the 10 ILs with a Stabinger viscometer from 263.15 K to 373.15 K at atmospheric pressure [5]. Density measurements up to 120 MPa up to 120 MPa were performed with a DMA HPM Anton Paar densimeter and from 278.15 to 398.15 K [7]. Viscosities for five of these ILs were measured for pressures up to 150 MPa and from 313 K to 363 K in a falling body viscometer. Thermal stabilities were measured for some the above ILs using thermogravimetric analysis in dynamic and isothermal modes in air and nitrogen atmosphere. Friction measurements of lubricated-surface contacts with several ILs and steel plates were conducted with a CSM standard tribometer. Wear volume was determined with a DEKTAK^3 profilometer.

Results and discussion: Analyzing the viscosities of our ILs at atmospheric pressure and those of the literature [3-5] we have found that the viscosity grade (kinematic viscosity in cSt at 40ºC) of the ionic liquids range from 10 to at least 460, which is an excellent range for the many applications of the lubricants and hydraulic fluids. We have also found several trends that can be used to tailor the ILs as lubricant of for other applications. Thus, the viscosity dependence with the anion type is:

$[NTf_2]^- < [(C_2F_5)_3PF_3]^- < [(C_2F_5SO_2)_2N]^- < [CF_3SO_3]^- < [BF_4]^- < [PF_6]^- < [C_2SO_4]^- < [C_1SO_4]^- < [C_6SO_4]^- < [CH_3COO]^- < Cl^- < Br^-$

ILs having highly symmetric or almost spherical anions are most viscous. ILs with a common anion and similar alkyl chain length, viscosity increases following the order. For imidazolium ILs, viscosity increases with the length of the alkyl chains. In general the viscosity follows the following anion trend: imidazolium < n-alkyl pyridinium < pyrrolidinium [4,5].

As regards the behaviour of the viscosity with temperature, it is considered that a good lubricant is that whose viscosity varies as little as possible with temperature. Thus, the effectiveness of lubrication and energy losses do not vary with external factors concerning the temperature. Lubricants with a high viscosity index (VI) show small changes in viscosity with temperature .VI of the commonly used lubricants ranges from 20 to 300 whereas for ILs in general ranges from 60 to 240 [3-5]. For the 10 ILs studied in this work the VI ranges 107 to 191.Higher viscosity indices were found for ILs with Tf_2N anion and $[C_1OC_2C_1Pyrr]$, $[C_2C_1im]$ and $[C_4C_1Pyrr]$ cations. The longer alkyl chains of imidazolium cations and of alkylsulfate anions the lower the VI, whereas for the ammonium and phosphonium cations VI increases with the length of alkyl chains [4-5].

From viscosity data at high pressures of ILs and other lubricants we have concluded [4,6] that the viscosity-pressure coefficient, α_{film}, of mineral oils are the highest. Synthetic and vegetable oils have similar α_{film} values, whereas those of ILs are the lowest except for $[C_1OC_2C_1Pyrr][FAP]$. Higher α_{film} values means higher film forming capability, so boundary wear is better avoided in gears. In contrast, low pressure-viscosity coefficients: save friction energy, reduce sub-surface stress and pressure peaks, so avoid wear and failure of gear elements and bearings. But the low film thickness could give wear problems [4,6].

Low isothermal compressibilities are favorable for hydraulic fluids and gear oils. Some ILs are twice less compressible than current hydraulic fluids. We have found the following trend with *the anion:*

$[(C_2F_5)_3PF_3]^- > [NTf_2]^- > [C_8SO_4]^- > [C_6SO_4]^- > [PF_6]^- > [BF_4]^- > [C_2SO_4]^-$

Besides, compressibilities increase with the alkyl chain length of the anions and also of the cations.

On the other hand, the decomposition temperatures of ILs the following anion trend

$[PF_6]^-$>[BETI]$^-$ >$[NTf_2]^-$>$[CF_3SO_3]^-$>[FAP]$^-$ >$[BF_4]^-$>I, Cl$^-$,Br, non-fluorinated anions as $[C_2SO_4]^-$ and $[C_6SO_4]^-$

The nature of the cation and the alkyl chain length have a small effect, although the **i**midazolium cations tend to be thermally more stable than the tetra-alkyl ammonium cations [1-4]. Dicationic ILs $[ROCH_2(C_1)_2im)_2]^{++}$ have a high thermal stability [1,2]. Nevertheless, it should point out that the definition of stability and of the maximum operation temperature is being an open question [3].

Concerning the friction and wear, ILs with [FAP]$^-$ and $[Tf_2N]^-$ have generally better anti-wear properties than those with $[BF_4]^-$ and $[PF_6]^-$, being ILs with [FAP]$^-$ better than $[Tf_2N]^-$ ILs. Most of the studies were performed with ILs with $[C_nC_1im]$ anions. Friction and wear diminish with the length of the alkyl chains. ILs with tetraalkylphosphonium or tetraalkylammonium cations present excellent tribological performance. New studies include methoxyalkylimidazolium trialkylmethoxy-ethylamonium, tetraalkyl-phosphonium, dicationic LIs, 4-methylbenzenesulfonate(tosylate), among others [1-4].

Conclusions: The structure influence on thermophysical and tribological properties was presented for several ILs. To create tailor-made lubricants and hydraulic fluids more studies are envisaged.

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