Deep Eutectic Solvents (DES) Based On Sulphur For Silicon Surfaces As Alternative Lubricants

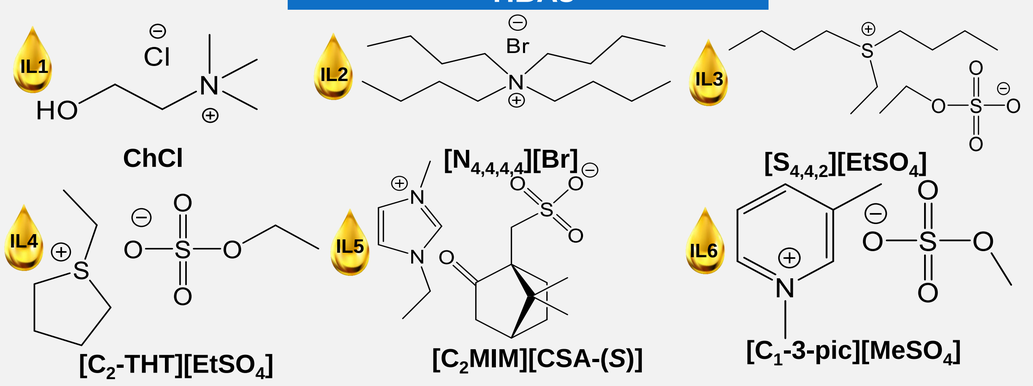
Mónica Antunes[a,b], Luís C. Branco*[b], Benilde Saramago*[a], Anne-Sophie Martins[a], Mariana de Sá Freire [a,b], Fernando Caetano[a,c], Hermínio Diogo[a], Rogério Colaço[d]

[a] Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[b] LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal,
[c] Universidade Aberta, R. da Escola Politécnica, 147, 1269-001 Lisboa, Portugal
[d] IDMEC-Instituto de Engenharia Mecânica, Departamento de Engenharia Mecânica, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.
* Corresponding authors: l.branco@fct.unl.pt; b.saramago@tecnico.ulisboa.pt

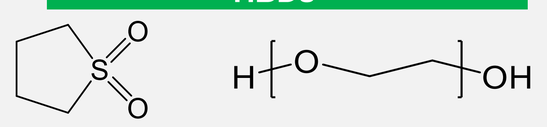
Introduction

- DESs composed by a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), have recently being proposed as possible "green" alternatives to mineral oils and ionic liquids (ILs) in the lubrication of steel surfaces.
- New DESs containing sulphur units in their structure were prepared and tested in the lubrication of silicon surfaces which are relevant for nano/microelectromechanical systems (NEMS/MEMS).
- Four new DESs were prepared: [$S_{4,4,2}$][$EtSO_4$]:PEG, [C_2-THT][$EtSO_4$]:PEG, [C_2MIM][(*S*)-CSA]:PEG, and [C_1-3-pic][$MeSO_4$]:PEG.
- Three already known DES, were tested for comparison purposes: tetrabutylammonium bromide: tetrahydrothiophene 1,1-dioxide ([$N_{4,4,4,4}$][Br]:Sulfolane), choline chloride: polyethylene glycol (ChCl:PEG), and tetrabutylammonium bromide: polyethylene glycol ([$N_{4,4,4,4}$][Br]:PEG).

HBAs

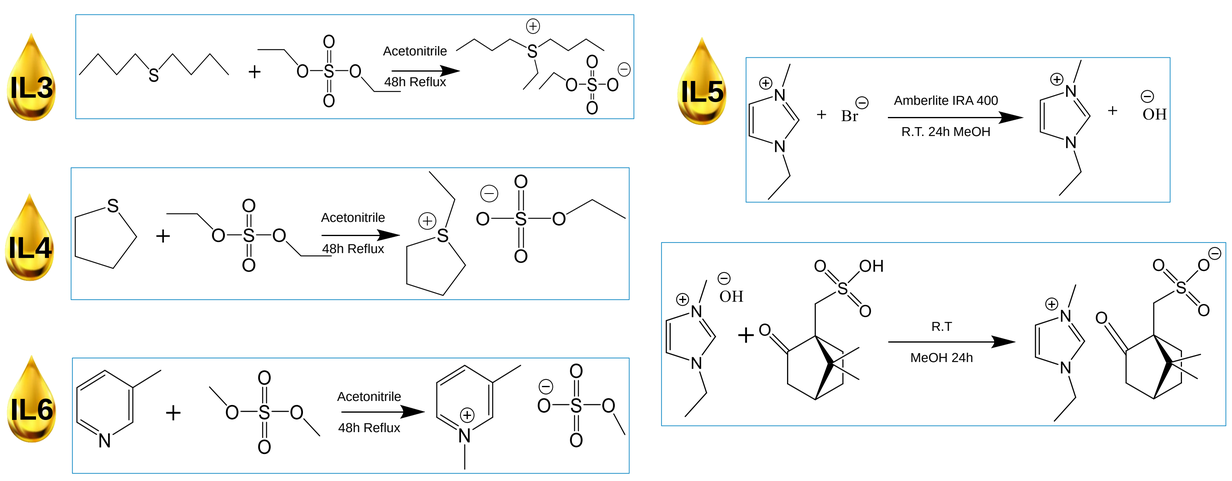


HBDs



ILs synthesis + DES preparation → Characterization of the DES: Calorimetry, wettability and viscosity → Tribological tests

ILs Synthesis



DES preparation

Proportion HBA:HBD 1:4 molar

Calorimetric Characterization (DSC)

Table 1: Thermal analysis of different DES and their components, including glass transition temperature (T_g), melting temperature (T_m) and C_p difference (ΔC_p).

Compound	(a) T_g(ºC) / (b)T_m (ºC)	ΔCp(J/g.ºC)
DES		
IL1:PEG	(a) -20[1]	-
IL2:Sulf	-(a)78.2	0.818
IL2:PEG	(a)-81.1	0.915
IL3:PEG	(a)-81.4	0.9802
IL4:PEG	(a)-80.7	0.914
IL5:PEG	(a)-76.3	1.024
IL6:PEG	(a)-74.2	0.933
DES Components		
IL1	(b) 302 [2]	-
IL2	(b) 103 [3]	-
Sulfolane	(b) 26 [4]	-
IL3	(a)-86.3	0.568
IL4	(a)-86.1	0.521
IL5	(a)-32.9	0.530
IL6	(a)-70.7	0.343
PEG	(a)-56 [5]	-

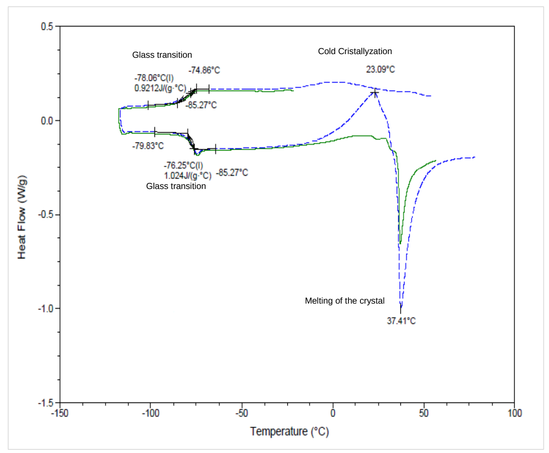


Figure 1: Example of a thermogram obtained with IL5:PEG: first cycle in blue (dashed line), second cycle in green (continuous line).

- The DESs did not reveal a melting temperature, instead a single glass transition temperature (T_g) was observed suggesting the formation of an eutectic mixture.
- With the exception of IL3:PEG and IL4:PEG, the values of T_g were lower than those of the pure components.
- The values of ΔC_p for the DESs are higher than those of the correspondent ILs which may be considered an advantage when using these liquids as lubricants in tribological processes where they can act as heat sinkers.

Wettability and Viscosity

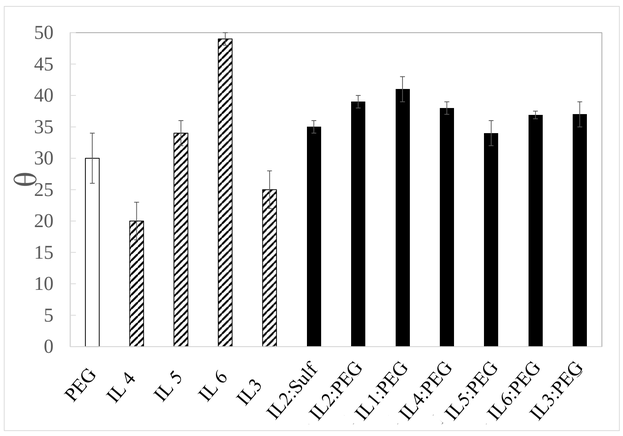
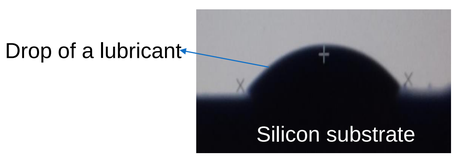


Figure 2: Contact angles of the liquids on silicon substrates

Table 2: Viscosity of the lubricants at 293 K

Compound	Viscosity (η) (mPa.s at 293 K)
DES	
IL1:PEG	122±3
IL2:Sulf	139±3
IL2:PEG	153±3
IL3:PEG	146±4
IL4:PEG	163.5±0.3
IL5:PEG	130.6±0.1
IL6:PEG	185.9±0.1
DES Components	
IL3	307±1
IL4	413±4
IL5	11506±20
IL6	14325±2
PEG	60±0.1

- All liquids present low contact angles, varying between 20º and 49º.
- All DESs are moderately viscous, although considerably more than PEG, which may constitute an advantage concerning their lubrication ability.
- Among the DESs, IL1:PEG is the less viscous fluid which may result from the low van der Waals interactions involving choline, the smallest cation, in agreement with its relatively high freezing temperature (-20ºC).



Tribological tests

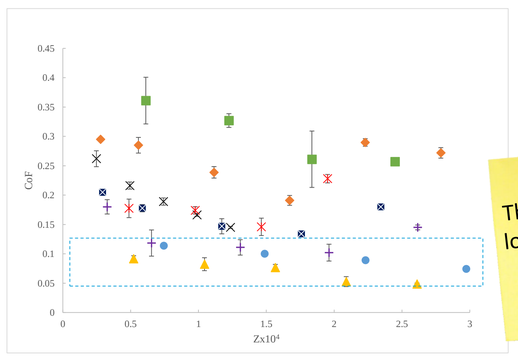


Figure 3: Plots of the friction coefficient (CoF) as a function of the Sommerfeld parameter,($Z=\frac{\eta v r}{F}$) , obtained with steel spheres sliding on silicon substrates using force 15mN and velocities between 4 and 20 m/s: ✕PEG; ✕ IL1:PEG; ◆IL2:Sulfolane; ■IL2:PEG; ⊠IL3:PEG; ✚ IL4:PEG; ▲IL5:PEG; ●IL6: PEG. The error bars correspond to standard deviations (n ≥ 4).

For the best DES (IL5:PEG and IL6:PEG) the CoFs of the HBA and HBD components were compared with that of the respective DES

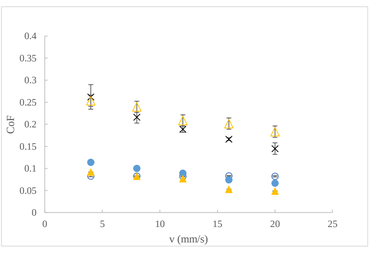


Figure 4: Plots of (CoF) as a function of velocity (v) , using force 15mN : ✕ PEG; ▲ IL5:PEG; ●IL6: PEG; △ IL5;◯IL6.

- The lubrication regime may be considered boundary/mixed (low Z). The load is carried mainly by the surface asperities or partially by the asperities and by the lubricant film.
- For PEG the lubrication regime is closer to boundary lubrication, since there is a decrease of the CoF when Z increases.
- The poor behavior of IL2:Sulfolane and IL2:PEG may be attributed to the star-like [$N_{4,4,4,4}$] cation hindering the formation of a stable tribofilm.

- The enhanced lubrication of IL5:PEG and IL6:PEG should be due to the interaction of S−O group in the anions with the Si surface yielding the Si−O−S bond.
- For IL6:PEG, the pure IL and the DES led to similar CoFs, meaning that the tribological performance of the mixture depends on the boundary layer rather than its viscosity .
- IL5 led to CoF values greater than PEG, while a significant decrease was observed with IL5:PEG. The poor tribological performance of IL5 may result from internal friction in the liquid.

Conclusions

- Four new DES containing S units were efficiently prepared and characterized.
- IL5 and IL6 containing sulfate or sulfonate anions combined with PEG lead to DESs with good lubrication properties of Si surfaces.
- The overall characteristics of these compounds indicate that they may constitute an advantageous alternative to the traditional oils in microelectronics lubrication.

References: **1-** Abbott, *el al.* V. WO 02/26701 (A2), 2002 (Scionix Limited). ; **2-**·Abbott, *el al*. *Chem. Commun.* 2003, 70-71 ; **3-** Alomar, M. K *el al*.. J. Mol. Liq. 2016, 215, 98-103. **4-**National Center for Biotechnology Information. PubChem Compound Database; CID=31347, https://pubchem.ncbi.nlm.nih.gov/compound/31347 (accessed Feb. 15, 2019).**5-**Majumdar, R *el al*. Pharmazie 2010, 65, 343–347.

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