THE ENERGETIC – SUPERFICIAL AND LUBRICITY PROPERTIES OF PETROLEUM PRODUCTS AND IONIC LIQUIDS

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Abstract

This paper presents the results of comparative investigations on the lubricity and energetic superficial properties of selected petroleum products and new ionic liquids (ILs). Three base oils from polish petroleum refinery (PAO–6, SN–650, SN–350) and lubricity additive (Additin RC2515 EP) have been investigated comparatively to four ionic liquids with imidazolium organic cations and different inorganic anions, i.e. bis (trifluoromethylsulfonyl) imide and tetrafluoroborate.

The lubricating ability properties petroleum products and ionic liquids have been assessed according to Polish Standard PN–76/C–04147 (ASTM D2596–69 and ASTM D2270–77) on Four–Ball Testing Machine. The investigation range of lubricity properties are limited to the assessment only two parameters i.e. $P_{(t)}$ – seizure load for increasing continuous loading and $G_{(oz)}$ – wear limiting load capacity. The superficial properties of oil compounds and ionic liquids have been assessed by means of modern KSV Sigma 701 Tensiometer. Surface tension σ and wetting angle θ were assessed. The obtained results confirmed the possibilities of using tested ionic liquids as lubricants. The best lubricity properties, close to properties of Additin RC2515, had 1–methyl– 3–oktyloxymethylimidazolium tetrafluoroborate.

Keywords: *boundary layer, lubricity, ionic liquids, surface tension, contact angle*

1. Introduction

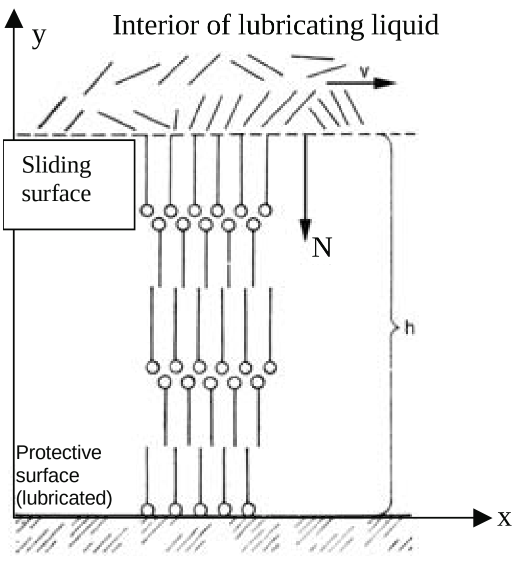

Fig. 1. Model of boundary layer: N–normal load, h–thickness of boundary layer, v–velocity of flowing of lubricating liquid

The most effective methods for the protection of elements in machines and motor vehicles against tribological wear out is to create very durable boundary lubricating film on their sliding surface, which is very resistant to the interaction of large normal and tangent loads. The stability of boundary film is the so–called measure of the lubricating ability (lubricity) of lubricants, which appears during boundary friction i.e. when the lubricated surface is protected by several molecular layers of lubricating liquid, which is located within the interaction non–saturation of intermolecular forces (Van der Waal's forces) of the lubricating surface. The field of action of these forces causes inducted polarization of molecules of grease and connected with their orientation, more often than parallel to the lines of action of those forces i.e. perpendicular to the lubricating surface (Fig. 1).

The lubricity is a set property i.e. it depends on the chemical constitution of lubricants, as well as, on the free surface energy of a lubricating surface and oils. In order to obtain a suitable quality of oil it inserts into the oils so–called lubricity additives i.e. anti–wear (AW) and anti–seizure (AS) additives. These substances must have properties of surfactants, which have adsorbing and chemisorbing abilities, as well as being characterized with a large dipole moment. As a result of this, these substances can ensure the creation of a stable boundary film on a lubricating surface, and therefore, obtaining a high lubricity of the oil, [4, 5]. There exists a close relationship between the free energy of the lubricating body and the surface tension and the wetting angle of the surfactant, which have to be friendly for environment. For this reason ionic liquids attract the interest of tribological scientists, [10].

Ionic liquids (ILs) belong to a group of chemical compounds from area the so–called "green chemistry". They are known inorganic chemistry also as a medium for many industrial chemical reactions [8, 9]. They are also used in electrochemistry (electrolysis, lithium cells, electrochemical condensers). Currently the "official" definition of ionic liquids uses the boiling point of water as a point of reference: Ionic liquids are ionic compounds, which are liquids below 100[°C]. But more commonly, ionic liquids have melting points below room temperature; some of them even have melting point below 0 [°C]. These materials are liquid over a wide temperature range (300-400°C) from the melting point to the decomposition temperature of ionic liquid. Therefore, ionic liquids are interesting substances as lubricants for many tribological junctions.

2. Investigation objects

Three organic base oils from petroleum refinery and selected high quality lubricity additive have been investigated in the first stage:

PAO–6: Polyalphaolefins – hydrogenated olefin oligomers manufactured by the catalytic polymeryzation of linear alphaolefins that have well defined, wax–free isoparaffinic structures, for blending of industrial oils,

SN–650 and SN–350: mineral base oils from vacuum distillation of atmosphere distillation residue of petroleum, for blending of industrial oils,

Additin RC2515 EP Additive: surfactant–lubricity additive sulphurized vegetable fatty oils and olefins, for blending of industrial oils which are working in extreme pressure conditions.

Comparatively to organic oils, four new ionic liquids with imidazolium organic cations and two different inorganic anions have been investigated:

1ILs: 1– methyl – 3 – oktyloxymethylimidazolium tetrafluoroborate ($C_{13}H_{25}BF_4N_2O$) from organic imidazolium cation $[C_{13}H_{25}N_2O]^+$ and inorganic anion $[BF_4]^-$,

2ILs: 1 – methyl – 3 – oktyloxymethylimidazolium bis(trifluoromethylsulfonyl)imide ($C_{15}H_{25}F_6N_3O_5S_2$) from organic imidazolium cation $[C_{13}H_{25}N_2O]^+$ and inorganic anion $[N(CF_3SO_2)_2]^-$**,**

3ILs: 1 – butoxymethyl – 3 – methylimidazolium bis(trifluoromethylsulfonyl)imide ($C_{11}H_{17}F_6N_3O_5S_2$) from organic imidazolium cation $[C_9H_{17}N_2O]^+$ and inorganic anion $[N(CF_3SO_2)_2]^-$**,**

4ILs: 1 – butoxymethyl – 3 – buthylimidazolium bis(trifluoromethylsulfonyl)imide ($C_{14}H_{23}F_6N_3O_5S_2$) from organic imidazolium cation $[C_{12}H_{23}N_2O]^+$ and inorganic anion $[N(CF_3SO_2)_2]^-$**,**

First ionic liquid (*1ILs*) and second ionic liquid (*2ILs*) have the same organic cation i.e. 1–methyl–3–oktyloxymethylimidazolium $[C_{13}H_{25}N_2O]^+$ and two different inorganic anions i.e. tetrafluoroboborate–$[BF_4]^-$ and bis(trifluoromethylsulfonyl)imide–$[N(CF_3SO_2)_2]^-$.

On the other hand, second (*2ILs*), third (*3ILs*) and fourth (*4ILs*) ionic liquids have the same inorganic anions i.e. bis(trifluoromethylsulfonyl)imide–$[N(CF3SO_2)_2]^-$ and three a little different organic imidazolium cations i.e. 1 – methyl – 3 – oktyloxymethylimidazolium $[C_{13}H_{25}N_2O]^+$; 1–butoxymethyl–3–methylimidazolium $[C_9H_{17}N_2O]^+$; 1–butoxymethyl–3–buthylimidazolium $[C_{12}H_{23}N_2O]^+$.

3. Range and methods of investigations

The energetic–superficial properties (surface tension σ and wetting angle θ) as well as the density ρ of oil compounds and ionic liquids have been assessed by means of modern and very sensitive KSV Sigma 701 Tensiometer (Fig.2), [3]. The kinematic viscosity ν and viscosity index VI appointed according to Polish Standard [6].

Fig. 2. KSV Sigma 701 Tensiometer for measurements of surface tension and contact angle

The lubricity properties of oil compound and ionic liquids have been assessed on Four–Ball Testing Machine (Fig. 3) according to Polish Standard [7], which is comfortable to ASME Standards [1,2].

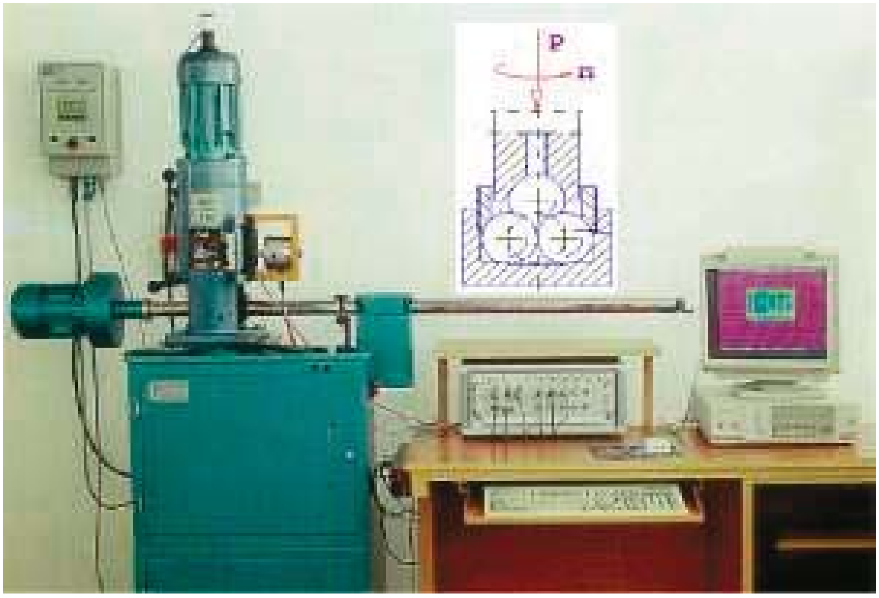

Fig. 3. KSV Sigma 701 Tensiometer for measurements of surface tension and contact angle

The investigation range of ionic liquids lubricity properties are limited to the assessment only two lubricating ability parameters i.e. $P_{(t)}$–seizure load for increasing continuous loading and G_{oz}–wear limiting load capacity. The assessment of $P_{(t)}$ is realized for a smoothly increasing load (41.667 daN/s) and G_{oz} under the constant load 150kG (147.15daN) for 60s [7].

4. Results of investigations and analysis

The values of tested energetic–superficial properties and lubricity properties of oil compounds and ionic liquids are shown below in Table 1.

Tab. 1. Collected parameters of tested lubricating liquids

Lubricants / Parameters	**PAO–6**	**SN–650**	**SN–350 (1114)**	**Additin RC2515 EP**	**1ILs**	**2ILs**	**3ILs**	**4ILs**
Density ρ [g/cm^3] at 25°C	0.816	0.881	0.876	0.881	1.12	1.32	1.43	1.33
Kinematic viscosity ν [mm^2/s] at 25°C	58.26	392.32	173.17	1597.91	495.00	78.00	47.00	54.00
at 40°C	30.78	135	75	631.00				
at 100°C	5.84	13.80	8.60	58.36				
Viscosity index VI	135	90	90					
Melting point t_{ms}°C					+ 10.8	– 34	– 40.7	– 45.9
solidific/pour point	< – 40	< – 9	< – 12					
Surface tension σ [mN/m] at 25°C	27.523	30.460	29.112	30.026	26.532	28.984	27.096	28.810
at 40°C	26.846	29.184	28.727	28.883	25.467	28.183	25.500	28.215
at 100°C	23.069	25.785	24.810	25.174	22.717	25.187	22.238	25.214
Contact angle θ [°] at 25°C	34.78	35.03	22.30	29.01	36.99	16.48	14.01	6.86
at 40°C	28.28	28.23	20.04	17.52	27.25	8.99	0.00	0.00
at 100°C	20.88	5.25	0.00	0.00	0.00	0.00	0.00	0.00
Seizure load incr. contin. $P_{(t)}$daN	71.58	157.1	131.54	304.71	261.7	175.9	184.0	182.0
Wear limit. load cap. G_{oz}daN/mm^2	44.99	274.4	268.3	371.31				

All tested lubricants, both components uses commonly for blending of industrial oils and ionic liquids, characterized good and very well wetting. In room temperature the contact angle θ amounted from 6.86[°] to 36.99[°] for tested ionic liquids (ILs) and from 22.30[°] to 35.03[°] for oil components, also for Additin RC2515 was 29.01[°]. The contact angles suddenly less during increasing temperature and in temperature 100[°C[almost all tested lubricants obtains θ~0[°C] (besides PAO–6) that means full wetting. The surface tensions σ of tested lubricants insignificant were different and had in room temperature for ionic liquids the values from 26.532[mN/m] to 28.984[mN/m] and for base oils from 22.30[mN/m] to 35.03[mN/m] and for surfactant Additin 30.026[mN/m]. The best lubricating ability properties determined by $P_{(t)}$ and G_{oz} parameters had Additin RC2515 EP, which adding to different oil bases (apart a lot of other additives) enables formation oils on good lubricating ability properties and viscosity–temperature properties, [2]. Among tested ionic liquids definitely the best lubricity properties, close to properties of Additin RC2515, characterized ionic liquid as *1ILs* with inorganic anion, $[BF_4]^-$. This ionic liquid had also the highest kinematic viscosity from among all lubricants, apart Additin RC2515. The other ionic liquids having inorganic anion $[N(CF_3SO_2)_2]^-$ and relatively low kinematic viscosities at 25[°C], comparable with viscosity of PAO–6, had worse lubricating ability properties relative to *1ILs* and Additin. However, all tested ionic liquids had better lubricity properties in comparison with the base oils.

In the Fig.4. and Fig. 5. are shown the characteristic functional dependences, which are made on the basis of the results collected in Table 1.

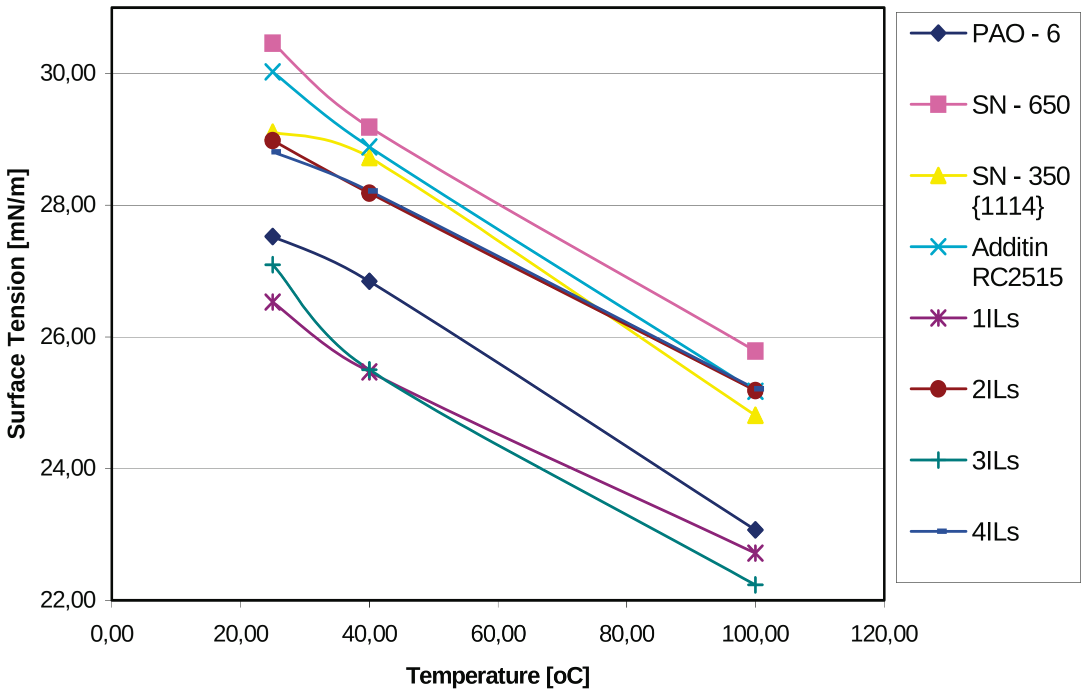

Fig .4. The surface tension of tested lubricants versus temperature

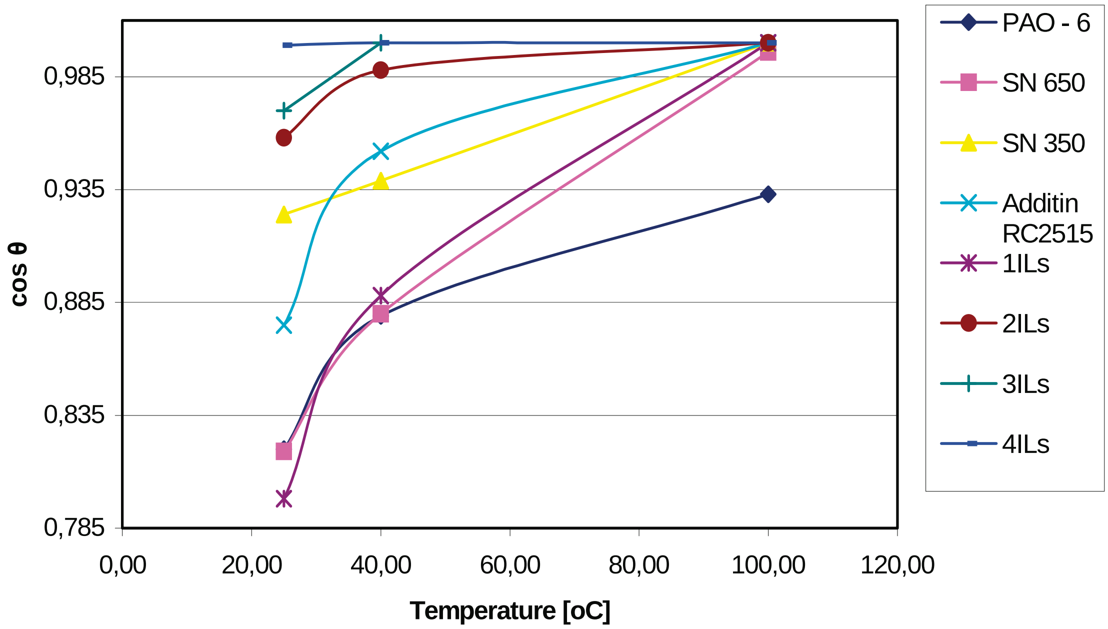

Fig. 5. The cosθ of tested lubricants versus temperature

5. Conclusion

- the obtained results confirmed the possibilities of using tested ionic liquids as a lubricants,
- the ionic liquids had the same surface tension as the oil compounds, but better wetting power,
- the 1ILs ionic liquids (with inorganic anion $[BF4]^{-}$) had the best lubricity properties characterized by parameters $P_{(t)}$ and $G_{(oz)}$,
- the conducted and described investigations are of pilot character and are to be continued.

Acknowledgments

This scientific work has been financed by Ministry of Science and High Education of the Republic of Poland from Found provided for scientific research (2007 – 2010) under development project Nr 0R00002904/PBR/15 – 249/2007/WAT and authors expressed their appreciation

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