SYNTHESIS, PHYSICOCHEMICAL, AND TRIBOLOGICAL PROPERTIES OF AMMONIUM BASED PROTIC IONIC LIQUIDS

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Abstract

Lubrication is one of the main features influencing both energy consumption and reliability of lubricated mechanisms. Recently ionic liquids became an attractive lubricating material, used as net lubricant or as additives. Protic ionic liquids have a potential in the field of lubrication because they consist of organic acids already having adsorption ability. In the present study we synthesized three ammonium based ionic liquids having different cations and the same anion. As cations t-octylamine, diethanolamine, dodecylamine were used, while oleic acid was employed as anion. During the synthesis corresponding ammonium salts were obtained. Physicochemical and tribological properties of the synthesized ionic liquids were investigated using them as additives in synthetic base oil. It was found that they have different appearance, viscosity and miscibility in the base oils. Despite difference in structure they possess similar tribological properties.

Key words: *protic ionic liquids, lubricants, lubricant additives, ammonium salts, friction*

1. INTRODUCTION

Industrial growth is accompanied by the development of new materials for various industrial uses. Lubricants are examples of such materials as they are widely used in all industrial sectors. About 85% of all the lubricants currently used in the world are oil-based oils. It is estimated that about 50% of all the lubricants used worldwide are released by accidental spillage. These oils pollute the soil, water and air, causing severe damage to various forms of life. Taking into account the growing human interference with the environment, the use of environmentally friendly materials in various industries, including lubrication, has gained a great deal of interest (Kamalakar et al. 2015).

Lubricants play a vital role in reducing friction between sliding parts, preventing mechanical failure and improving energy efficiency. Modern lubricants consist of functional additives such as viscosity modifiers or viscosity index improvers, friction and wear reducing agents, dispersants, depressants, antioxidant blended in the base oil (Bapat et al. 2018, Zhang et al. 2018).

Ionic liquids can also be assigned as functional additives. Already since 2001 there are articles that explore the potential use of ionic liquids (IL) for lubrication. Over the next decade, many studies used IL as a neat lubricants or lubricant additives (García et al. 2014; Minami 2009).

Ionic liquids are liquid organic salts. Like classic metal salts, IL is a neutral compound composed of anion and cation. Inorganic salts have a low melting point (<100 °C). Ionic liquids, which are in a liquid state at room temperature, were called "room temperature IL" (Welton 1999). The low melting temperature of these compounds is due to the fact that these compounds consist of relatively high nitrogen or phosphorus-containing asymmetric organic cation and a weakly coordinated inorganic or organic anion. Different combinations of anion and cation form a large class of these compounds. It is estimated that number of such compounds with different properties can be as high as 10^{18} (Carmichael & Seddon 2000). The uniqueness of IL is also determined by the fact that the change in anion and / or cation changes the physical and chemical properties of the IL, so they are also called "modelled solvents" (Wasserscheid & Welton 2003).

They have unique physical and chemical properties, such as inherent polarity (ions) for strong surface adsorption, low flammability, high thermal stability, and low sensitivity in rheological behavior to

environmental changes compared to conventional oil lubricants (García et al. 2014; Arias-Pardilla, Espinosa & Bermúdez 2015; Amiril, Rahim & Syahrullail 2017).

Despite the good physical and chemical properties of IL, their use as neat lubricants is economically ineffective due to their high cost. There are several scattered studies that looked at the possibility of using IL as an additive, but encountered a major technical barrier that most of the previously investigated ILs had - very low solubility in conventional non-polar hydrocarbon lubricating oils (<< 1%) (Minami 2009; Viesca et al. 2017; Arias-Pardilla, Espinosa & Bermúdez 2015). This breakthrough took place in 2012 when the use of oil soluble IL as an additive to improve anti-scuffing / anti-wear properties was first reported. Since then, using IL as a lubricant additive has become a new lubrication topic (Bapat et al. 2018; Oulego et al. 2018).

The purpose of this work is to synthesize carboxylic quaternary ammonium salts and to investigate their properties using as lubricant additives.

2. MATERIALS AND METHODS

2.1. Materials used

Materials used for the synthesis of protolytic ionic liquids (PILS): *tert*-octylamine (95%), diethanolamine (≥ 98.0%), dodecylamine (98%) from ACROS organics and oleic acid (90%) from Sigma-Aldrich. Polyalphaolefin (PAO 4) was used as synthetic base oil.

2.2. Synthesis of PILS

Ionic liquids are organic salts composed of anions and cations. In the synthesis of ionic liquids, amino compounds are used as bases of Brionsted, and organic acids as Brionstedic acids. Amino alkylation is a direct reaction between an ammonium cation and an anion of a carboxylic acid (oleic acid).

a) with primary amine:

$$\underset{\text{oleic acid (OA)}}{CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH} + \underset{\text{primary amine}}{RNH_2} \longrightarrow$$

$$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-\overset{-}{C}OO\overset{+}{N}H_3-R$$

OA-NH_3^+ complexes

b) with secondary amine:

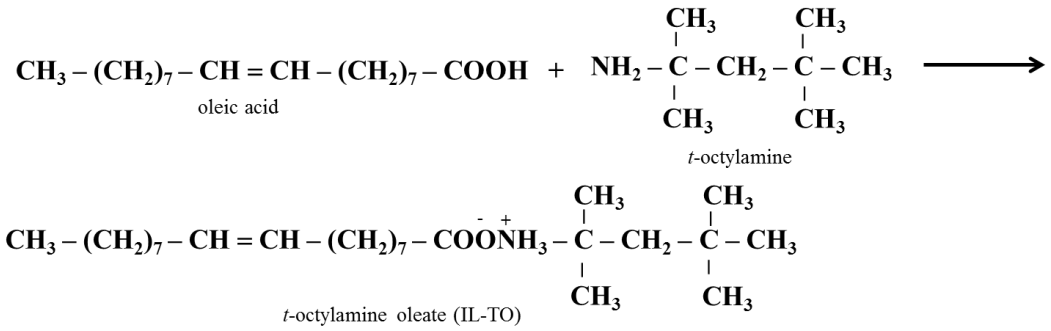
$$\underset{\text{oleic acid (OR)}}{CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH} + \underset{\text{secondary amine}}{R_2NH} \longrightarrow$$

$$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-\overset{-}{C}OO\overset{+}{N}H_2-R_2$$

OA-NH_2^+ complexes

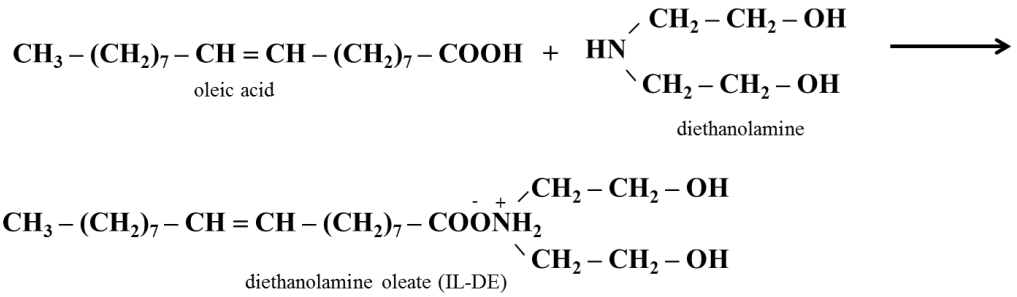
The synthesis was carried out in a thermostated three-necked flask equipped with a reflux condenser, a thermometer and a dropping funnel. The acid was added dropwise into the amine (6 drops/min). Heated amine compound vigorously stirred (400 rpm). The initial reaction temperature depends on the alkylation agent of the amino compound. During the synthesis, the acid-base neutralization reaction takes place and a protic ionic liquid (PILS) is formed.

❖ Synthesis of *t*-octhylamine oleate:



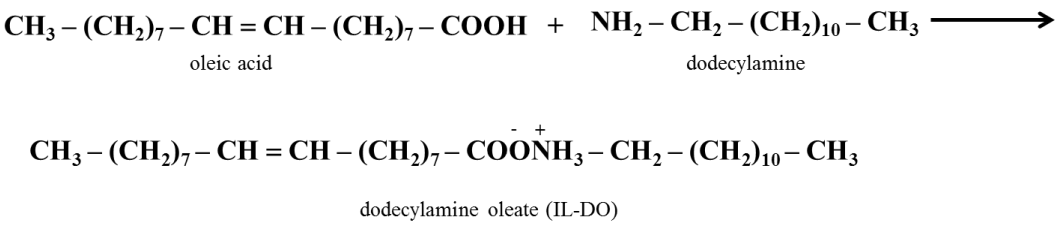
Initial reaction is performed at room temperature (~ 22 °C) at a molar ratio of 1: 1 *t*-octylamine to oleic acid. When the whole acid is added, the temperature is increased to 80 °C.

❖ Synthesis of diethanolamine oleate:



Initial reaction is performed at 80 °C, with a 1:1 molar ratio of diethanolamine to oleic acid. When the whole acid is added, the reaction was performed keeping the same temperature.

❖ Synthesis of dodecylamine oleate:



As in the case of diethanolamine oleate initial reaction is performed at 80 °C, with a 1:1 molar ratio of diethanolamine to oleic acid. When the whole acid is added, the reaction was performed keeping the same temperature. The process of alkylation of amines was carried out for 24 h starting when the acid was added.

2.3. Evaluation of formation of ionic liquid

Formation of IL was confirmed by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra were taken by a PerkinElmer Spectrum RXI spectrometer. Scanning was set to the range of 4000-800 cm^{-1}, with scanning intervals of 1 cm^{-1} and resolution 4 cm^{-1}.

2.4. Viscosity and acid number evaluation

The dynamic viscosity was measured according to standard EN ISO 3104+AC. Dynamic-viscosity measurements were performed in a Stabinger Viscometer, model SVM 3000 (Anton Paar, Austria). The viscosity index was calculated using ISO 2909:2002 method.

Acid number studies were performed according to the requirements of EN ISO 660 standard test method.

2.5. Sample preparation

By using ionic liquids as additives in the synthetic base oil PAO 4, they were weighed to the nearest 0.1 mg according to the calculated concentration. The ionic liquid concentrations of 0.5; 1; 2.5 and 5 % by wt. in base oil were chosen. Blending of ionic liquids in base oil was carried out with a magnetic stirrer for 30 minute at 60 °C and 500 rpm.

2.6. *Evaluation of solubility of ionic liquid in the base oil*

IL solubility in the base oil was accomplished using a visual detection method. The solubility was detected by the appearance of a precipitate. The solubility measurements were carried out at room temperature. The prepared samples were placed into a micro-centrifuge at 10,000 rpm for 15 min. The oil-IL blends were examined under bright lighting for evidence of separation or cloudiness right after centrifuge and 24 h after. Triplicates of each sample were measured.

2.7. Tribological properties evaluation

Tribological tests were performed on ball-on-plate configuration at reciprocating motion. The test scheme is presented in Fig. 1. The 6 mm bearing steel E-52100 ball, having surface roughness of 0.05 µm and hardness of 58-66 HRC, was slid against the plate made of the same steel having surface roughness of 0.02 µm and hardness of 190-200 HV30. Before the test balls, plates, and all the appropriate parts were cleaned in ultrasonic bath in toluene and acetone. Tribological test conditions are as follows: load - 4 N; stroke length - 1 mm; reciprocation frequency - 15Hz; test duration – 30 min; test temperature - 30 °C. The friction coefficient was continuously recorded during the test and given as a result. Its values were also used to calculate mean coefficient of friction. At least two replicates were made for each prepared sample.

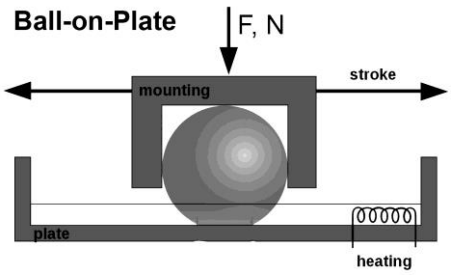


Fig. 1. Ball-on-plate type tribometer

3. RESULTS AND DISCUSSION

Evaluation of formation of ionic liquid. Three ammonium ionic liquids with different cation structures but the same anion structure were investigated. They are *t*-octhylamine oleate (IL-TO), diethanolamine oleate (IL-DE), dodecylamine oleate (IL-DO). Fourier transform infrared spectroscopy was performed to identify the structure of protic ionic liquids as shown in Fig. 2 (A-C).

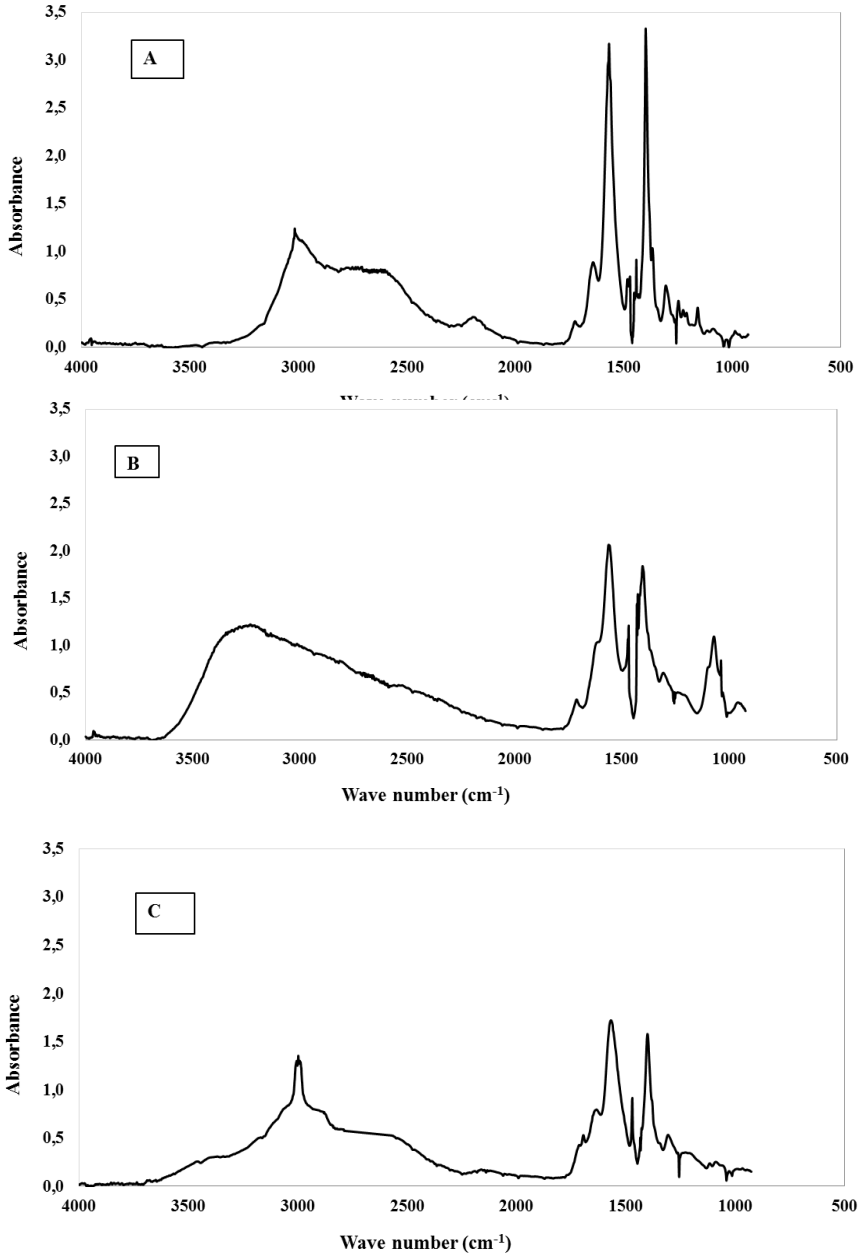


Fig. 2. FTIR spectra of (A) – IL-TO; (B) – IL-DE; (C) – IL-DO ionic liquids in the spectral range 4000-500 cm^{-1}

The results of the FTIR analysis are very similar for the synthesized protic ionic liquids (PILS). The broad band in the range of 3500…2250 cm^{-1} is characteristic of the ammonium structure. The OH stretching vibration is embedded in this band. Adsorption maxima in 1536 cm^{-1} was assigned to NH_3^+ of primary amine salt. Due to the fact, that there was marginal or no absorption band at 1725 cm^{-1} it is confirmed that all the oleic acid was reacted.

After synthesis the appearance of PILS was evaluated. They have dark yellow color. At room temperature IL-TO - was liquid, IL-DO and IL-DE – semisolids.

Evaluation of solubility. Due to the identical anion structure among the three ILs, changes in oil solubility are governed solely by the cation structures. The results showed that solubility of ionic liquids depends on the number of carbon atoms in the cation alkyl groups. Increasing the number of

carbon atoms in the cation increases the solubility in base oil. These results are in the line with the results found by other scientists (Barnhill et al. 2014). The lowest solubility in poly-alpha-olefin was demonstrated by IL-DE. Its solubility in base oil was only ≤ 0.5 %. Solubility of IL with ammonium cations containing 8 (t-octhylamine) and 12 carbon (dodecylamine) atoms was similar. Solubility of both IL-TO and IL-DO in PAO4 was ≥ 5 %.

Viscosity and acid number evaluation. The viscosity of liquids and liquid mixtures is a complex feature that depends on temperature. This is especially true for ionic liquids and their mixtures. The viscosity of IL is highly dependent on the type of cation and anion and is significantly higher than that of conventional oils. Viscosity of pure ionic liquids at room temperature can be as low as ≤ 10 mPa·s or as high as ≥ 1000 mPa·s. The average dynamic viscosity values as a function of temperature for the ionic liquids blends of 0.5; 1; 2.5 and 5 % by wt. in base oil are shown in Fig. 3 (A-C) and Fig. 4 (A-D).

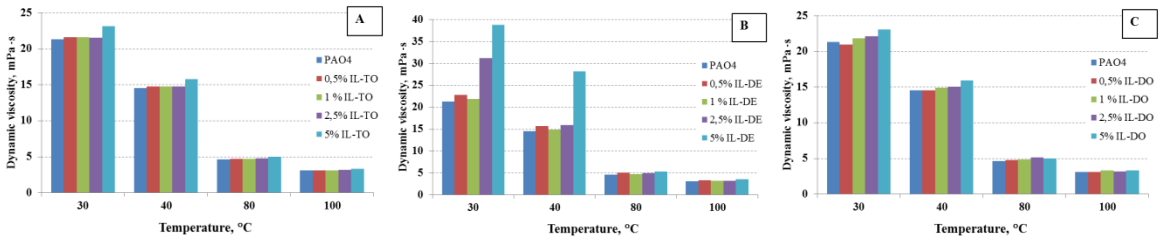


Fig. 3. Viscosity of the ionic liquids ((A) – IL-TO; (B) – IL-DE; (C) – IL-DO) concentrations of 0.5; 1; 2.5 and 5 % by wt. in base oil

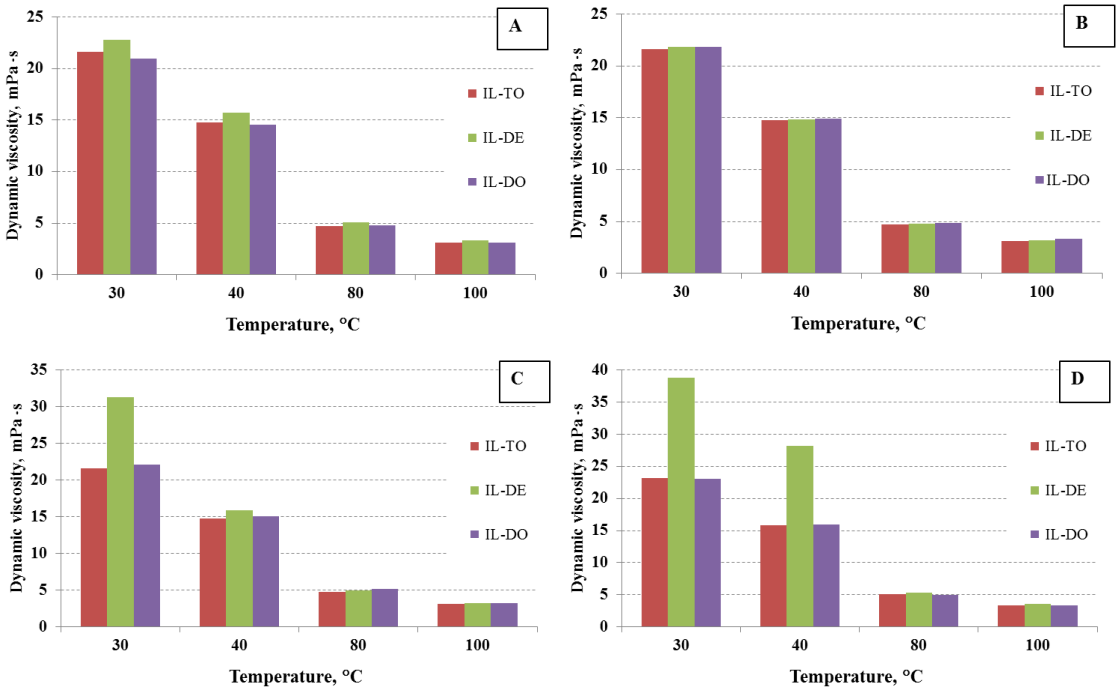


Fig. 4. Viscosity of the ionic liquids concentrations of (A) 0.5; (B) 1; (C) 2.5 and (D) 5 % by wt. in base oil

It can be observed that the dynamic viscosity decreases with increasing temperature. The results show (Fig. 3 and 4) that increasing the concentration of IL in PAO4 results in a marginally increased dynamic viscosity of the mixture. At 0.5 and 1 % IL (Fig. 4 A, B) concentrations in the mixture with poly-alpha-olefin, the dynamic viscosity of all tested mixtures at different temperatures is similar to each other. Only the 2.5 and 5 % concentrations of IL-DE ionic liquid in PAO4 were more distinct

(Fig. 4 C, D). Their dynamic viscosity is 1.5-2 times higher compared to other tested ionic fluid mixtures.

Viscosity Index - assesses oil viscosity dependence on temperature. The higher the viscosity index, the higher the lubricating efficiency of the oil. It is calculated using two oil viscosities at 100 °C and 40 °C. Table 1 presents the experimental density (ρ) data of protic ionic liquids concentrations of 0.5; 1; 2.5 and 5 % by wt. in base oil at 23 °C temperature and the viscosity index (VI). At low concentration PILS possess similar viscosity index which is governed by VI of PAO4. Increasing amount of PILS in the base oil leads to decreased VI for IL-DE and IL-DO. Addition of IL-TO in PAO4 do not changes its VI.

Table 1. Density (ρ), the viscosity index (VI) and acid number (AN) of the blend of the ionic liquids with PAO4

	0.5% IL-TO	**1% IL-TO**	**2.5% IL-TO**	**5% IL-TO**
$\rho_{23\,°C}$, kg · m^{-3}	811	811	812	813
VI	125	129	124	124
AN, mgKOH · g^{-1}	0.58	1.16	2.89	5.79
	0.5% IL-DE	**1% IL-DE**	**2.5% IL-DE**	**5% IL-DE**
$\rho_{23\,°C}$, kg · m^{-3}	816	811	814	817
VI	131	127	126	102
AN, mgKOH · g^{-1}	0.49	0.98	2.46	4.92
	0.5% IL-DO	**1% IL-DO**	**2.5% IL-DO**	**5% IL-DO**
$\rho_{23\,°C}$, kg · m^{-3}	810	811	811	813
VI	138	128	125	127
AN, mgKOH · g^{-1}	0.51	1.03	2.54	5.04

Acid number for prepared mixtures is governed by amount of added ionic liquid. With increasing PILS concentration acid number proportionally increases. Its values are similar for all investigated PILS. However addition of IL-DE leads to lower acid number. The highest acidity has base oil mixture with IL-TO.

Friction evaluation. The influence of PILS concentration in base oil on coefficient of friction is presented in Fig. 5. It was observed that main change is induced by the smallest investigated amount of PILS. Only 0.5 % of PILS is enough to reduce friction coefficient by 30 %. Further increase has marginal effect on friction. All the investigated PILS possess similar friction reduction properties. Only the small difference can be discern at lower concentrations where IL-TO has better performance. With increasing amount of PILS in base oil there performance becomes equal.

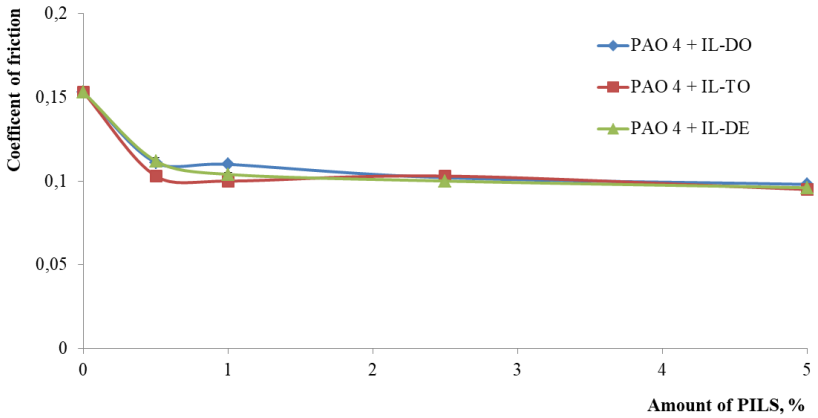
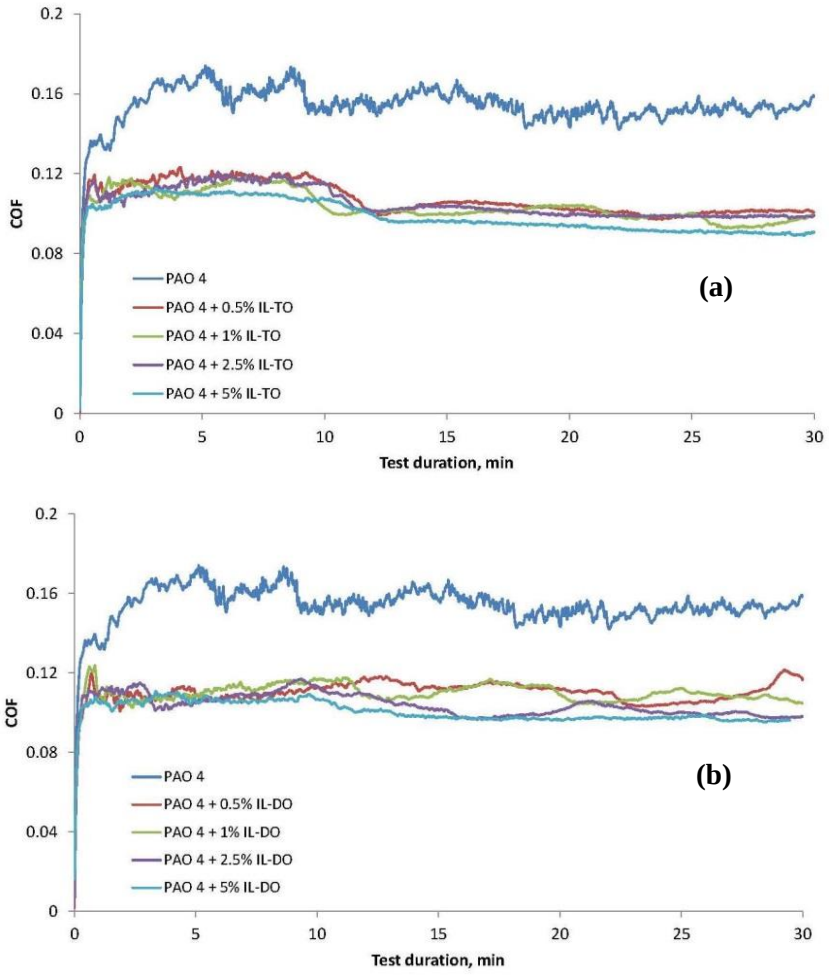


Fig. 5. Influence of PILS concentration in base oil on mean friction coefficient

Friction variation curves recorded during the tribological tests are presented in Fig. 6. It is clear that presents of PILS in the synthetic base oil substantially improves its friction reduction ability. The base oil lubricated friction pair possess high and unstable friction coefficient exceeding 0.170. Such value is typical for intensive abrasion and adhesive wear. PILS loaded base oil has lower (les then 0.100) and more stable friction coefficient. It means that friction conditions were changed substantially. All the samples possess similar tendency: some fluctuation at the run-in stage; even and low steady state friction. The predicted friction reduction mechanism is adsorption layer which is well known to have low friction and is dominant in ionic liquid lubricated friction pairs.



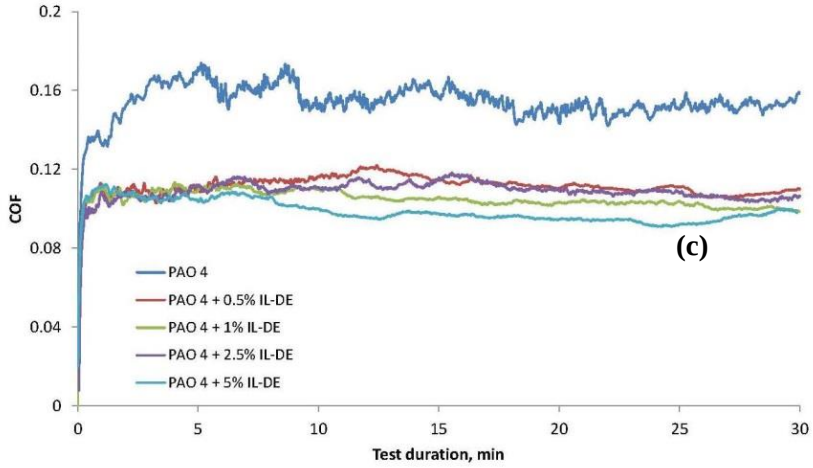


Fig. 6. Friction variation during the tribological test when lubricating with IL-TO (a), IL-DO (b), and IL-DE (c) blends in PAO 4 base oil

CONCLUSIONS

A new composites consisting of protic ionic liquids were synthesized. They are *t*-octhylamine oleate, diethanolamine oleate, dodecylamine oleate. In this study they were used as additives in synthetic base oil. It was found that blending PAO4 with PILS has only marginal effect on its dynamic viscosity and density. With increasing concentration of IL-DO and IL-DE viscosity index of final mixture decreased. Tribological properties of investigated blends are similar. Blending of PAO4 with PILS can improve its friction reduction ability up to 30 %. At low concentration IL-TO has better friction reduction properties, moreover its steady state friction is more stable. The predicted friction reduction mechanism is adsorbtion layer.

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