

## An alternative method for the desulfurization of hydrocarbon fuels

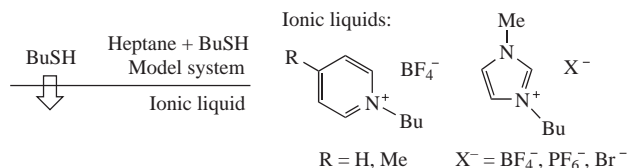
Alexandra V. Okhlobystina,<sup>\*a</sup> Andrei O. Okhlobystin,<sup>a</sup> Natalia N. Letichevskaya,<sup>a</sup>  
Vasilya F. Abdulaeva,<sup>a</sup> Natalia O. Movchan<sup>b</sup> and Nadezhda T. Berberova<sup>a</sup>

<sup>a</sup> Astrakhan State Technical University, 414025 Astrakhan, Russian Federation. E-mail: ionradical@gmail.com

<sup>b</sup> Southern Scientific Centre of the Russian Academy of Sciences, 344006 Rostov-on-Don, Russian Federation

DOI: 10.1016/j.mencom.2017.01.035

**Conditions for the extraction of sulfur compounds from model hydrocarbon mixtures and real fuels (gasoline and fuel oil) with pyridinium and imidazolium ionic liquids were optimized to provide the maximum degree of desulfurization of fuels.**



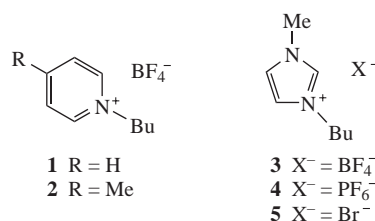
Ionic liquids are of considerable current interest due to a unique set of their properties: a wide range of occurrence in a liquid state, low vapor pressure, low flammability, high electrical conductivity and a good ability to dissolve inorganic, organic and organometallic compounds and gases.<sup>1</sup> They are used in organic synthesis, catalysis, analytical chemistry and the development of new composite materials.<sup>2–5</sup> At the same time, examples of the use of ionic liquids in electrochemistry are scarce. Meanwhile, the extraction of thiophene series substances from hydrocarbon solutions with ionic liquids was described.<sup>6,7</sup> The ability of ionic liquids to extract polar compounds from nonpolar hydrocarbon fluids is very attractive as applied to the desulfurization of commercial oil products.

Previously,<sup>8</sup> the recovery of sulfur compounds from model hydrocarbon mixtures using extraction with pyridinium ionic liquids was reported. In this work, we studied the extraction of sulfur compounds in more detail with the use of not only pyridinium but also imidazolium ionic liquids.

Here, we used gas chromatography with a capillary column and a flame-photometric detector for the identification of sulfur compounds. Columns with ionic liquids as an active phase are produced on an industrial scale (BASF) since 2008. This is a high-polarity column phase based on imidazolium salts with volumetric cations and anions, a combination of which allows one to reach the required selectivity. The advantages of the Russian chromatographic columns with ionic liquids<sup>9</sup> are the increased selectivity and ability to work at temperatures up to 270 °C.<sup>10</sup>

The practical significance of the work consists in the possibility of using the experimental data in new technologies for the desulfurization of distillate and hydrotreated fractions of crude oils based on a combination process of the selective oxidation of sulfur compounds followed by the removal of polar products.

We used the following salts: 1-butylpyridinium tetrafluoroborate **1**, 1-butyl-4-methylpyridinium tetrafluoroborate **2** and



1-butyl-3-methylimidazole salts with the anions BF<sub>4</sub><sup>-</sup> (**3**), PF<sub>6</sub><sup>-</sup> (**4**) and Br<sup>-</sup> (**5**). Ionic liquid **1** was prepared according to a published procedure.<sup>11,12</sup> Ionic liquids **2–5** were purchased from Sigma Aldrich. The model mixtures were the solutions of butyl mercaptan (I), benzyl mercaptan (II), thiophene (III), diethyl sulfide (IV) and *n*-butyl disulfide (V) in *n*-heptane with a sulfur component concentration of 100 ppm.<sup>†</sup>

The viscosity of ionic melts decreases with temperature; this is accompanied by an increase in the diffusion coefficient and the electrical conductivity.<sup>13</sup> Thus, special attention was paid to optimizing temperature for the extraction of sulfur impurities and a ratio between the ionic liquid and the hydrocarbon mixture. Upon the addition of ionic liquids **1–4** to model mixtures I–III, the formation of a two-phase system was observed.

A comparative analysis of the influence of the cation and anion of the ionic liquid on its absorption capacity was performed. The sulfur-removing properties decreased in the order BF<sub>4</sub><sup>-</sup> > Br<sup>-</sup> > PF<sub>6</sub><sup>-</sup> and in the order [BMIIm]<sup>+</sup> > [BMPy]<sup>+</sup> > [BPY]<sup>+</sup>. Ionic liquids **3–5** exhibited the greatest desulfurizing ability (the degrees of extraction of butyl mercaptan were 30, 26 and 50%, and the degrees of extraction of benzyl mercaptan were 58, 38 and 45%, respectively) in one extraction cycle. An increase in the number of extraction cycles up to three (30 min each) resulted in the almost complete extraction of sulfur impurities, and their content decreased from 100 to 11 ppm (model mixture II), which corresponds to a 98% degree of extraction.

The optimum range of extraction temperatures was 40–50 °C; the hydrocarbon mixture:ionic liquid ratio was 1:1, and the optimal extraction time was 20–25 min.

<sup>†</sup> Extraction was carried out for 20–30 min with constant stirring in glass tubes using an extraction facility and a mechanical shaker. The degree of extraction of sulfur compounds from hydrocarbon mixtures was monitored by X-ray fluorescence analysis on an ASE-1 instrument to determine the sulfur content of oil products. The GLC of sulfur compounds was conducted on a Crystal Lux 4000 chromatograph with a flame photometric detector and an SLB-IL111 capillary column (15 m × 0.1 mm, 0.08 μm) from the active phase (ionic liquid) 1,5-di(2,3-dimethylimidazolium)-pentane bis(trifluoromethylsulfonyl)imide under temperature-programming conditions. Stepwise extraction or fractionation using a tenfold volume of acetonitrile at a temperature of 70 °C and a pressure of 70 mbar was carried out for the regeneration of ionic liquids. The time of one extraction cycle was 1–2 min.

**Table 1** Degrees of extraction of sulfur compounds by ionic liquid **4**.

Sulfur compound in model fuel	Degree of extraction (%)
<i>n</i> -Butyl mercaptan	27
Benzyl mercaptan	38
<i>n</i> -Butyl disulfide	31
Diethyl sulfide	16

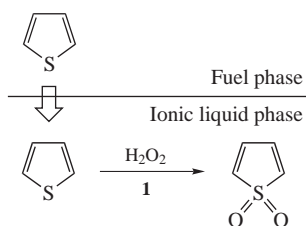
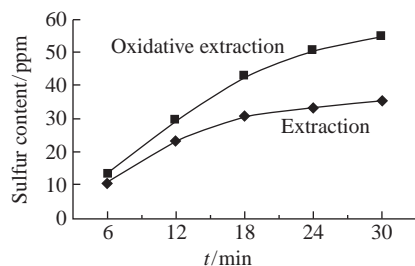
We studied the selectivity of ionic liquids, for example, salt **4**, for different classes of organic sulfur compounds in light distillation fractions using model motor fuels I, II, IV, and V. The concentration of sulfur compounds in a model mixture was 100 ppm. The extraction time was 20 min; the temperature was 40 °C, and the model fuel: ionic liquid weight ratio was 1 : 1. As a result, the maximum residual concentration of organic sulfur compounds was observed in the raffinate containing diethyl sulfide (Table 1). The desulfurizing ability of ionic liquid **4** decreased in the order aromatic mercaptans > disulfides > > aliphatic mercaptans > sulfides.

To increase the degree of extraction of low-polarity thiophene from model mixture III, the oxidative extraction with hydrogen peroxide was used, leading to the formation of polar sulfur oxides (Figures 1 and 2). As a result, 26% thiophene can be extracted with conventional extraction in a single cycle, and 37% when the oxidative extraction was used. In both cases, ionic liquid **1** was applied.

The positive results of a study of the extraction properties of ionic liquids for model fuels allowed us to examine the desulfurization process in real media: distillate fractions IBP-120, 120–230 and 180–350 hydrotreated fraction of the Astrakhan gas condensate *via* ionic liquid **2**. As the result of a one-step extraction, the sulfur contents of the fractions IBP-120, 120–230 and 180–350 decreased from 1636 to 1290 ppm, from 4781 to 4534 ppm and from 240 to 155 ppm, respectively. The degrees of extraction were 21, 5 and 35%, respectively. After two additional extraction cycles for fractions 120–230, the sulfur concentration decreased to 3998 ppm (16%). The main process parameters of the extraction of sulfur-containing impurities from hydrocarbons were as follows: temperature, 55 °C; contact time, 30 min; and selective solvent to raw materials ratio, 1 : 1.

For ionic liquid **2**, multistep extraction from hydrotreated fraction 180–350 was performed (Table 2).

The results of the desulfurization of fuel oil are given in Table 3. The most efficient extraction (3.3% → 2.6%) was achieved in contact with ionic liquid **3** for 30 min at 40 °C and a weight

**Figure 1** The fuel and ionic-liquid phases in oxidative extraction.**Figure 2** Sulfur content vs. extraction time.**Table 2** Multistep extraction of diesel fraction.<sup>a</sup>

Step of extraction	Sulfur content/ppm	Degree of extraction (%)
1–3	92	62
3–6	50	79
6–9	12	95

<sup>a</sup>Temperature, 55 °C; mixing time, 30 min. Ionic liquid **2** to fuel weight ratio, 1 : 1. Original sulfur content of the fuel, 240 ppm.

**Table 3** Extraction desulfurization of fuel oil by ionic liquids.<sup>a</sup>

Ionic liquid	Degree of extraction (%)	T/°C	Mixing time/min
<b>1</b>	19	55	30
<b>3</b>	22	40	30
<b>5</b>	10	85	15

<sup>a</sup>Ionic liquid to fuel weight ratio, 1 : 1.

ratio of 1 : 1. Note that it was difficult to perform phase separation of ionic liquids and heavy hydrocarbon fractions during the experiment. This problem was avoided by contact with salt **5**.

In conclusion, the extraction properties of ionic liquids **1–5** for the extraction of sulfur compounds from model mixtures I–III were estimated. Temperature, concentration and time parameters of effective desulfurization of model fuels were optimized. The testing of pyridinium and imidazolium salts showed that they are the effective extractants of sulfur impurities from hydrocarbon fractions.

Note that the ionic liquid with the bromide anion is a good extractant. At room temperature, it is solid, but when heated from 50 to 80 °C it becomes liquid and easy to extract. The main attraction is that the separation of the extractant is very effective on cooling the mixture of the extractant and the extracted mixture to room temperature.

This work was supported by the Russian Foundation for Basic Research (grant no. 14-03-31930 mol\_a) and the Russian President (grant no. MK-2943.2015.3).

## References

- E. V. Pavlechko, *Khimicheskie problemy sozdaniya novykh materialov i tekhnologii (Chemical Problems of Creating New Materials and Technologies)*, Belarus State University, Minsk, 2008 (in Russian).
- A. S. Kucherenko, V. V. Perepelkin, G. M. Zhdankina, G. V. Kryshal, E. Srinivasan, H. Inani and S. G. Zlotin, *Mendeleev Commun.*, 2016, **26**, 388.
- M. A. Epishina, A. S. Kulikov and N. V. Ignat'ev, M. Schulte and N. N. Makhova, *Mendeleev Commun.*, 2015, **25**, 41.
- S. V. Kochetov, A. S. Kucherenko and S. G. Zlotin, *Mendeleev Commun.*, 2015, **25**, 168.
- L. L. Fershtat, S. S. Ashirbaev, A. S. Kulikov, V. V. Kachala and N. N. Makhova, *Mendeleev Commun.*, 2015, **25**, 257.
- X. Chen, S. Yuan, A. A. Abdeltawab, S. S. Al-Deyab, J. Zhang, L. Yu and G. Yu, *Sep. Purif. Technol.*, 2014, **133**, 187.
- A. Bösmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz and P. Wasserscheid, *Chem. Commun.*, 2001, 2494.
- V. V. Okhlobystina, A. O. Okhlobystin, Yu. Yu. Koldaeva, N. O. Movchan, A. A. Litvin and N. T. Berberova, *Russ. J. Gen. Chem.*, 2013, **83**, 2062 (*Zh. Obshch. Khim.*, 2013, **83**, 1868).
- M. V. Shashkov, V. N. Sidelnikov and P. A. Zaikin, *Russ. J. Phys. Chem. A*, 2014, **88**, 717 (*Zh. Fiz. Khim.*, 2014, **88**, 714).
- S. Rodríguez-Sánchez, P. Galindo-Iranzo, A. C. Soria, M. L. Sanz, J. E. Quintanilla-López and R. Lebrón-Aguilar, *J. Chromatogr. A*, 2014, **1326**, 96.
- J. Zhang and A. Bond, *Analyst*, 2005, **130**, 1132.
- Z. Karpinski, C. Nanjundiah and R. A. Osteryoung, *Inorg. Chem.*, 1984, **23**, 3358.
- N. V. Shvedene, M. Yu. Nemilova, K. S. Khachatryan, N. A. Mamonov, A. V. Shukhaev, A. A. Formanovskii and I. V. Pletnev, *Vestn. Mosk. Univ., Ser. Khim.*, 2004, **45**, 324 (in Russian).

Received: 29th April 2016; Com. 16/4924