

## TASK-SPECIFIC IONIC LIQUIDS FOR EXTRACTIVE DESULPHURIZATION OF DIESEL FUEL

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**Abstract.** Task-specific ionic liquids based on imidazolium cation containing carbonitrile, carboxyl, and alkyl chains have been employed in an attempt to design new functionalized liquids for solvent extraction of sulphur compounds from diesel fuel.

**Keywords:** task-specific ionic liquids, extractive desulphurization, diesel fuel.

### Introduction

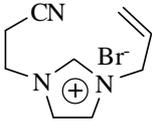
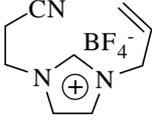
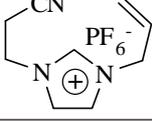
Many concepts and technologies have been developed during the last 20 years to desulphurize the least reactive sulphur species from the diesel feed in order to effectively reach the near zero sulphur content at attainable costs [1]. Functionalized ionic liquids are relatively cheap, easy to synthesize, have no measurable vapor pressure and can be competitive with conventional solvents and adopted in many industrial applications [2]. Hence, there is considerable interest in using them in place of volatile organic solvents for new production technology of ultra-low sulphur petroleum fractions. It is known that the presence of sulphur in heavy fuel oils leads to emission of  $\text{SO}_x$  which endangers public health [1]. It is worth noting that environmental regulations focus attention on reduction of emissions from the transport sector with the purpose of improving air quality [3]. Moreover, according to the European Union regulation, gasoline and diesel fuels should not exceed 10 ppm of total sulphur content starting from 2010 [4]. A current desulphurizing technology has included adsorptive desulphurization, hydrodesulphurization, oxidative desulphurization and extractive desulphurization. The last one is preferred over other separation methods for its advantages in less costly and easier disposal, since it incurs no chemical consumption or byproduct formation unlike other chemical methods [1]. Ionic liquids as selective extraction agents of different compounds were discussed earlier due to their novelty and theoretical interest [2, 5-27]. This prompted us to find new compounds having a carbonitrile, carboxyl and alkyl functional groups attached to an imidazolium cation. These compounds can be considered task-specific ionic liquids and can be useful for the removal of sulphur-containing compounds from the diesel fuel. In order to obtain new extractors, a number of ionic liquids were prepared from 1*H*-imidazole and studied for application in desulphurization of diesel fuel.

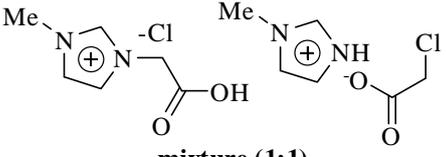
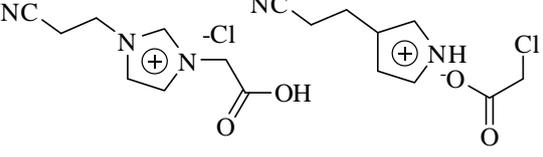
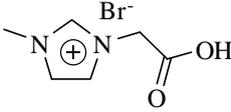
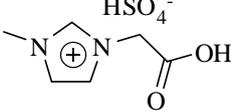
### Results and discussion

Previously, various types of ionic liquids were employed in the extractive desulphurization of diesel fuel because of their properties, such as immiscibility with fuels, high affinity to sulphur-containing substances, low volatility and high thermal stability [5-27]. Task-specific ionic liquids **1-8** used in this study were reported by us previously [28-31].

Table 1.

Degree of diesel desulphurization in dependence on the ionic liquid used.

No. Compound	Structure	Ref.	Degree of desulphurization (%)
1		28	65
2		28	68
3		28	69

4	 mixture (1:1)	29	88
5	 mixture (1:1)	29	87
6		30	54
7		30	78
8	$[\text{Fe}_3\text{O}(\text{H}_3\text{C}-\text{C}_3\text{H}_3\text{N}_2-\text{COO})_6(\text{H}_2\text{O})_3](\text{FeCl}_4)_7$	31	100

As shown in the table 1, the imidazolium-based molten salts **1-8** have functional groups like carbonitrile, carboxyl, and alkyl group, along with different anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{HSO}_4^-$ ,  $\text{FeCl}_4^-$ ). Firstly, the extraction ability of allyl- and carbonitrile- substituted ionic liquids **1-3** was evaluated for removal of sulphur species from the model diesel fuel. It was found that efficiency of extractive desulphurization of substances **1-3** was up to 65-69%. The effect of the chain substituent on imidazolium ring was also investigated. Desulphurization with task-specific ionic liquids **4** and **5** clearly exhibited much higher extraction ability than ionic liquids **1-3**. For a comparison, performances of the specific ionic liquids with protonated and coordinated carboxyl group were tested for extractive desulphurization. However, the extraction ability of ionic liquid **6** was lower than that of the corresponding mixture **4**. The reason for a higher extraction ability of **4** is not clear. The highest extractive desulphurization was obtained with task-specific ionic liquid **7** that exists as liquid at room temperature like mixtures **5** and **6**. Desulphurization in the presence of metal containing ionic liquid **8** with  $\text{FeCl}_4^-$  anions and  $\{\text{Fe}^{\text{III}}\text{O}\}$  cationic core clearly demonstrated that all the sulphur substances were completely extracted from the diesel fuel.

We believe that extractive desulphurization of diesel fuel is based on the fact that sulphur-containing compounds are more soluble in task-specific ionic liquids than in hydrocarbons. It is worth noting that such approach can be realized under ambient conditions.

## Conclusions

The reported data represent a straightforward procedure for the efficient and facile extractive desulphurization of the diesel fuel with task-specific ionic liquids. The procedure has remarkable practical utility because of its simplicity and the applied functionalized ionic liquids are relatively cheap and easy to synthesize. The studies on the extractive desulphurization of underground water with application of task-specific ionic liquids are underway in our laboratory.

## Experimental methods

Task-specific ionic liquids **1-8** were prepared using the methods [28-31]. Desulphurization experiments were conducted in 15 mL tubes. Task-specific ionic liquids were added into the model diesel fuel containing 0.06% of sulphur species. The weight ration of specific ionic liquid/model diesel fuel was set at 1:4. After mixing with 1200 rotation per minute for 6 hours, diesel fuel was removed by filtration (in case **1-3** and **6**) or decantation (in case **4, 5, 7** and **8**). Determination of sulphur content by lamp method was realized according to the GOST 19121-73 [32]. 1 mL of diesel fuel was diluted with 3 mL of n-heptane and incinerated in a burner-lamp connected to absorber (filled with 10 mL of  $\text{Na}_2\text{CO}_3$  water solution) at reduced pressure (90 mm of the mercury column). Afterwards, the lamp was washed with 1 mL of n-heptane and it was fully incinerated in duplicate. Water solution of  $\text{Na}_2\text{CO}_3$  from the absorber, containing

sulphur oxides, is then coloured with methylene orange and is titrated with HCl solution until the colour changes into the pink. The mass fraction of the sulphur is then determined according to the following equation:

$$X = \frac{(V - V_1) \cdot K \cdot 0.0008 \cdot 100}{m}$$

where,  $V$ - volume, mL of 0.05 N solution of HCl, used for titration of the control probe;  $V_1$ - volume, mL of 0.05 N solution of HCl, used for titration of the probe after incineration and absorption;  $K$ -correction factor to the titre of 0.05 N solution of HCl; 0.0008- weight of sulphur, equivalent to 1 mL of 0.05 N solution of HCl, g;  $m$ - weight of the probe, g. The result of the determination is expressed as the arithmetical mean of 2 parallel experiments.

### Acknowledgments

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