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# Application of Ionic Liquids for Extraction and Synthesis of Organosulfur Compounds

**V. V. Okhlobystina[a], A. O. Okhlobystin[a], Yu. Yu. Koldaeva[a], N. O. Movchan[b], A. A. Litvin[a], and N. T. Berberova[a]**

[a] *Astrakhan State Technical University, ul. Tatishcheva 16, Astrakhan, 414025 Russia*
*e-mail: ionradical@gmail.com*

[b] *Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, Russia*

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**Abstract**—We consider the possible application of pyridinium ionic liquids to desulfurize hydrocarbon raw products and to transform the extracted toxic admixtures into promising sulfur compounds. Anodic oxidation of the extracted thiols as well as oxidation in the presence of electron mediators (*N,N,N′,N′*-tetramethyl-1,4-phenylenediamine, tri-*p*-bromophenylamine, and tri-*p*-tolylamine) leads to the corresponding disulfides.

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Due to approval of the new fuel standards, development of approaches to eliminate residual admixtures of highly toxic thiols from hydrocarbon mixtures has become an important issue. Ionic liquids have been recognized as promising extractants of thiols from nonpolar media [1].

Ionic liquids have been discovered quite recently [2, 3]. These compounds consisting of bulky organic cation and inorganic or organic anion have revealed a set of unique properties. The asymmetric structure and spatial separation of the charges favor the formation of ion-containing liquid phase. This phase is stable over wide temperature range, showing low melting point and vapor pressure in combination with electrochemical stability and electric conductance. Owning to high polarity, some ionic liquids are not mixed with hydrocarbons, rather giving two- or multiphase systems, thus capable of extracting the polar admixtures from hydrocarbons [1, 2]. Ionic liquids are considered “green” solvents, as they are not flammable, non-toxic, non-explosive, and environmentally friendly.

Ionic liquids are promising for electrochemical studies as well, due to high electric conductivity and wide range of polarization potential [4].

Electron mediators are special catalytic systems, they are not consumed in the chemical processes and thus can be applied in tiny quantity [5]. The interest to electron mediators has emerged due to their ability to significantly decrease the activation energy of certain reactions [6, 7].

In this study, we considered the possible application of ionic liquids for extraction of thiols and their transformation into non-toxic disulfides via anodic oxidation of cation-radicals, including the processes in the presence of electron mediators. The following ionic liquids were studied: 1-butylpyridinium tetrafluoroborate **I** prepared according to [8, 9] and 1-butyl-4-methylpyridinium tetrafluoroborate **II** (Aldrich). Aromatic amines were used as electron mediators: (tri-*p*-tolylamine, tri-*p*-bromophenylamine, and *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine).

One of the most important characteristics of a solvent for electrochemical study is its electrochemical window, the difference between potentials of anodic and cathode redox reaction of background electrolyte [10]. We determined that the electrochemical window of the ionic liquids **I** and **II** was of 5.1 V and 5.4 V, respectively (Fig. 1).

The study of electrochemical properties of the ferrocene/ferrocenium redox pair in ionic liquids **I** and **II** revealed that the oxidation potentials were slightly shifted as compared to standard potentials of the same system in acetonitrile. In particular (Table 1), in the acetonitrile solution {0.1 mol/L of $[Bu_4N]ClO_4$)}, the anodic peak of ferrocene was of $E_{pa}$ = 0.42 V, the cathode peak potential $E_{pc}$ = 0.37 V, their difference being of $\Delta E$ = 0.058 V, $I_{pc}/I_{pa}$ = 1.00. In the ionic liquids **I** and **II**, for ferrocene $E_{pa}$ = 0.44 V, $E_{pc}$ = 0.41 V, $\Delta E$ = 0.033 V, and $I_{pc}/I_{pa}$ = 1.00. The results were in line with the published data that demonstrated the close potentials of ferrocene redox pair oxidation in the acetonitrile solution of $[Bu_4N][PF_6]$ and in a variety of ionic liquids [11–13]. Oxidation of ferrocene in acetonitrile as well as in the ionic liquids was completely reversible, as confirmed by the values of $\Delta E$ and $I_{pc}/I_{pa}$. However, in the cases of thiols the solvent effect on the potentials was more significant (see Table 1).

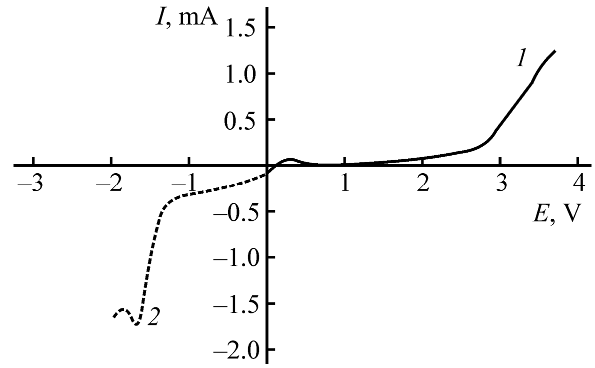



**Fig. 1.** Cyclic voltammogram of the (*1*) cathode branch (oxidation) and (*2*) anodic branch (reduction) of **II** (Pt-anode, Ag/AgCl).

Rheological studies of ionic liquids demonstrated that addition of water significantly changed the ionic liquid viscosity and, thus, the sensitivity of electrochemical determination of various species in ionic liquid media. Furthermore, Pt electrode was found sensitive to traces of water in the ionic liquids; that was revealed as a maximum around 1.30 V [14, 15]. The influence of water on oxidation of *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine in 1-methyl-3-[2,6-(*S*)-dimethyloctene-2-yl]imidazolium tetrafluoroborate was studied in [16]. It was found that the presence of water (5%) in *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine significantly increased the oxidation current. The influence of water on the ionic liquids viscosity was confirmed by determination of the diffusion coefficients.

We found that in the anhydrous ionic liquid the sensitivity of $C_4H_9SH$ determination ($E$ = 1.8 V in the ionic liquid) was decreased by 20 times. The effect was ascribed to the diffusion limitations in the case of viscous ionic liquid.

Thus, the effect of water on the ionic liquids properties was ambiguous. Addition of water enhanced the diffusion of the species in the ionic liquid. At the same time, the water impurity in the ionic liquid complicated the electrochemical identification. In the cyclic voltammogram of ionic liquid I with admixture of water, the oxidation peak at 1.27 V was observed, thus the identification of species at 1–2 V was poorer than in the case of dry solvent.

Extraction properties of ionic liquids **I** and **II** were studied using a model of heptane with admixture of thiols ($C_4H_9SH$, $C_7H_{15}SH$, $C_6H_5CH_2SH$, and others). After addition of **I** or **II** to that model mixture, a heterogeneous system was formed. After extraction (30 min, continuous stirring), the residual content of the thiols was determined with X-ray fluorescence sulfur analyzer (Fig. 2). It was to be seen that the extraction of aromatic thiol was twice as efficient as of the aliphatic thiol.

Further, the effect of temperature of the extraction degree of thiols was studied. Increasing the extraction temperature to 55°C led to more than 2-fold increase of the thiols recovery, mainly due to decrease of the ionic liquid viscosity and, consequently, diffusion

**Table 1.** Electrochemical parameters of thiols and disulfides (υ 200 mV/s, Ag/AgCl, $c$ $5\times10^{-3}$ mol/L, Pt)

| Solvent/background | $E_{pa}$ (RSH), V | | $E_{pa}$ (RSSR), V | |
|---|---|---|---|---|
| | $C_4H_9SH$ | $C_6H_5CH_2SH$ | $C_4H_9SSC_4H_9$ | $C_6H_5CH_2SSCH_2C_6H_5$ |
| $CH_2Cl_2$/0.1 mol/L $[Bu_4N]ClO_4$ | 1.70 | 1.76 | 1.40 | 1.27 |
| $CH_3CN$/0.1 mol/L $[Bu_4N]ClO_4$ | 1.62 | 1.72 | 1.32 | 1.43 |
| **I** or **II** | 1.83 | 1.98 | 1.28 | 1.65 |

**Table 2.** Electrochemical parameters of the organic mediators and the induced decrease of oxidation potential of $C_4H_9SH$ and $C_6H_5CH_2SH$ (υ 200 mV/s, Ag/AgCl, *c* 5×$10^{-3}$ mol/L, Pt)[a]

| Mediator | $E_{pa}$, V | | $\Delta E^*$, V | |
|---|---|---|---|---|
| | $CH_2Cl_2$/0.1 mol/L $[Bu_4N]ClO_4$ | **II** | $C_4H_9SH$ | $C_6H_5CH_2SH$ |
| Tri-*p*-tolylamine | 0.84 | 0.90 | 0.97 | 1.08 |
| Tri-*p*-bromophenylamine | 1.20 | 1.25 | 0.62 | 0.73 |
| *N,N,N′,N′*-Tetramethyl-1,4-phenylenediamine | 0.20; 0.80 | 0.25; 0.85 | 1.02 | 1.13 |

[a] $E_{pa}$, oxidation potentials; $\Delta E^* = E_R - E_M$; $E_M$, mediator oxidation potential; $E_R$, thiol oxidation potential.

enhancement. Above 55°C, thiols recovery from the model mixture decreased.

Electrolysis of $C_4H_9SH$ in ionic liquids **I** and **II** was studied at the potential of 1.80 V. Analysis of the electrolysis products revealed two oxidation peaks at the cyclic voltammogram, with $E'_{pa}$ of 1.28 V and 1.87 V, assigned to dibutyldisulfide and butanthiol-1, respectively. The introduction of additional amount of the reference samples of the assigned substances increased the peaks height, thus confirming the assignment (Fig. 3).

The mechanism of thiol oxidation in ionic liquid was similar to that in the classical solvents (acetonitrile or methylene chloride).

$$RSH \xrightarrow{-\bar{e},\ [BuPy]BF_4} RSH^{\bullet+} \xrightarrow[-2H^+]{[BuPy]BF_4} RS^{\bullet} + RS^{\bullet} \xrightarrow{[BuPy]BF_4} RS{-}SR$$

Thus, electrochemical oxidation of thiols allowed their conversion into non-toxic disulfides under environmentally friendly conditions.

In the next part of the study we investigated the possibility to decrease the energy consumed for the thiols oxidation by using electron mediators.

Electrochemical oxidation of thiols $C_4H_9SH$, $C_7H_{15}SH$, $C_6H_5CH_2SH$ in the ionic liquid was performed at the oxidation potential of the corresponding mediator (Table 2). Slight deviation of the mediator oxidation potential in the ionic liquid as compared to that in methylene chloride was observed.

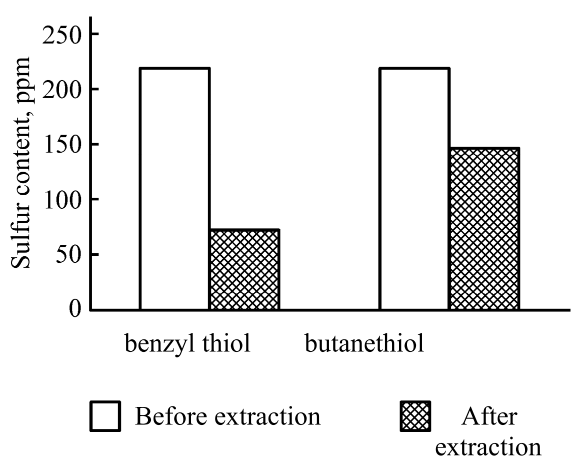



**Fig. 2.** Change of sulfur content in the model hydrocarbon mixtures containing benzyl thiol and butanethiol.

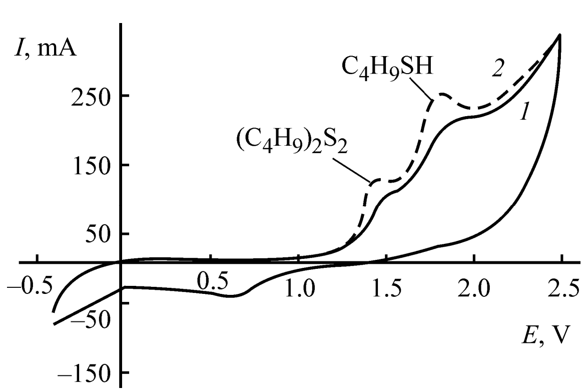
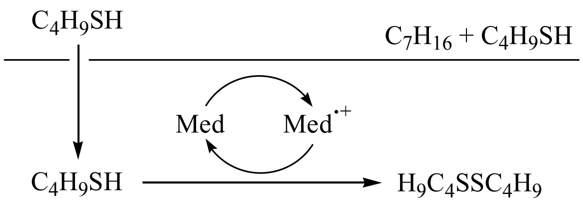



**Fig. 3.** Cyclic voltammogram of the products of electrolysis of α-butanethiol in (*1*) **II** and (*2*) with standard samples (Pt-anode, Ag/AgCl).

From Tables 1 and 2 it is to be seen that the oxidation potential of the electron mediators was significantly less than that of thiols ($C_4H_9SH$, $C_6H_5CH_2SH$), therefore, the electrochemical process overvoltage was decreased by $\Delta E^*$.

Electrolysis of $C_4H_9SH$ in the presence of *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine at constant potential of 0.90 V in the ionic liquid **II** led to decrease of the thiol content due to its dimerization into $H_9C_4SSC_4H_9$, as confirmed by the oxidation current in the registered cyclic voltammograms.

Using the heptane-butanethiol as a model example, the scheme of desulfurization with using ionic liquid and mediator (Med) is as follows.




Indeed, thiols could be extracted with ionic liquids and further converted into disulfides in the same medium.

## EXPERIMENTAL

Oxidation potentials were measured by cyclic voltammetry in the three-electrode cell with VersaSTAT 3 potentiostat. Working electrode: Pt ($S$ = 3.14 $mm^2$), auxiliary electrode: Pt ($S$ = 70 $mm^2$), comparative electrode: Ag/AgCl/KCl with waterproof diaphragm. Background electrolyte, [NBu4]$ClO_4$ was dried under reduced pressure during 48 h at 50°C. The mediators used (tri-*p*-tolylamine, tri-*p*-bromophenylamine, and *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine) were purchased from Aldrich, 99% grade. Preparative electrolysis was performed at stationary Pt plate electrodes ($S$ = 700 $mm^2$) in a 100 mL three-electrode cell without diaphragm.

**Ionic liquid I** [8, 9]. Pyridine (0.20 mol), 1-bromobutane (0.20 mol), and cyclohexane (50 mL) were stirred at 60°C during 12 h. White precipitate of *N*-butylpyridinium bromide was filtered off and dried in vacuum oven. Then, *N*-butylpyridinium bromide (0.20 mol) was mixed with sodium tetrafluoroborate (0.20 mol) in 100 mL of acetone, and stirred at room temperature during 12 h. The precipitate was filtered off, the solvent was then evaporated.

## ACKNOWLEDGMENTS

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