

On the Influence of Additives of Polymer, Sodium Nitrate, and 1-Methyl-2-Pyrrolidone on the Extraction of Thiophene in an *n*-Hexan–Water System

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Abstract—The effect of individual and multicomponent additives—water-soluble polymers (polyethylene glycol 400, polypropylene glycol 425, and polyvinylpyrrolidone 3500), sodium nitrate, and 1-methyl-2-pyrrolidone—on the extraction of thiophene in an *n*-hexane–water system has been studied. It is found that, in most cases, the introduction of small amounts of additives into the extraction system leads to a significant increase in the degree of extraction of thiophene from *n*-hexane in the aqueous phase in comparison with the individual components.

Keywords: liquid–liquid equilibrium, extraction, thiophene, water-soluble polymers, sodium nitrate, 1-methyl-2-pyrrolidone, *n*-hexane, light hydrocarbon fractions

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INTRODUCTION

The traditional method of the desulfurization of light hydrocarbon fractions is hydrotreatment [1]. This process allows one to effectively remove the aliphatic sulfur compound, although it requires high temperature, high pressure, expensive catalysts, and the constant use of a large amount of hydrogen [1, 2]. The use of this process for extracting polycyclic sulfur-containing compounds is economically and energetically disadvantageous. To solve such problems, alternative methods have been developed for the desulfurization of light hydrocarbon fractions, such as adsorption [3, 4], oxidation [5], and extraction [6–8], among which extraction is the most promising. This method is suitable for the extraction of a wide class of sulfur-containing compounds, including the isolation of thiophene and its derivatives. The advantages of extraction include minimum energy and economic costs due to the simplicity of the equipment and the fact that the process takes place at room temperature and atmospheric pressure.

Among the solvents used in the extraction desulfurization processes, N, N-dimethylformamide, acetonitrile, and sulfolane are used most often. One of the traditional extractants used in the desulfurization process of light hydrocarbon fractions is 1-methyl-2-pyrrolidone [9–11]. In the middle of the 20th century, it was established as an effective extractant with high selectivity with respect to sulfur-containing com-

pounds. It has been proven that 1-methyl-2-pyrrolidone extracts 99.4% of thiophene and its derivatives. However, due to its toxicity and flammability, its use negatively affects the environment and human health. The solution to these problems can be found through the use of more environmentally friendly extractants.

Along with traditional extractants in the desulfurization process of light hydrocarbon fractions, water-soluble polymers may also be used. To date, a significant number of studies have been carried out on the synthesis of extraction systems based on water-soluble polymers and their application for solving the problems of extracting organic substances [6, 7, 12–21], including for the desulfurization of light hydrocarbon fractions. Their main advantages are nontoxicity, low cost, and environmental safety. The authors of [21] studied the influence of the nature of such a polymer introduced into the *n*-hexane–water system on the extraction behavior of thiophene. The dependence of the efficiency of thiophene extraction into the polymer phase on the concentration of polyethylene glycol 400 (PEG-400), polypropylene glycol 425 (PPG-425), and polyvinylpyrrolidone 3500 (PVP-3500) was obtained. It was found that, with an increase in the polymer concentration in the *n*-hexane–water system, an increase in the distribution coefficient of thiophene is observed. Therefore, at a concentration of PEG-400 and PPG-425 of more than 80%, the degree of extraction of thiophene increases exponentially. It was

noted that the use of the studied polymers in the *n*-hexane–water system is promising in the process of purifying light hydrocarbon fractions from sulfur-containing compounds.

A number of inorganic salts were considered as effective and environmentally friendly extractants [22, 23]. In [22], the effect of sodium chloride and calcium chloride on the extraction of a number of heterocyclic sulfur compounds, including thiophene and its derivatives, was studied. As a result of the experiments, it was found that, with an increase in the salt content in the solution, the extractability of thiophene increases. The authors of [23] showed that the extraction efficiency of thiophene and its derivatives in the isoocane–water system can be significantly increased by introducing organic and inorganic acids, alkalis, and inorganic salts. Thus, the introduction of 15 wt % sulfuric acid allows you to remove thiophene at 52.6%; 10 wt % hydrochloric acid allows you to remove 50%; 3.5 wt % nitric acid, 47.2%; 3.5 wt % acetic acid, 44.4%; 10 wt % sodium chloride, 40%; 10 wt % ammonium hydroxide, 36%; and 10 wt % sodium hydroxide, 30.8%. Also, the authors of [23] noted that extraction systems containing sodium nitrate are promising in the process of desulfurization of light hydrocarbon fractions.

It is well known that often the use of mixtures of extractants can lead to a significant increase in distribution coefficients compared with additive values, which can be used to increase the efficiency of extraction and concentration. It is likely that the use of mixtures of extractants in heterogeneous systems based on water-soluble polymers can also have a positive effect. Thus, the aim of this work was to study the effect of introducing individual and multicomponent additives of various natures (polyethylene glycol 400, polypropylene glycol 425, polyvinylpyrrolidone 3500, sodium nitrate, and 1-methyl-2-pyrrolidone (NMP) *n*-hexane–water—simulating a solution of light hydrocarbon fractions) on the efficiency of thiophene extraction.

EXPERIMENTAL

When conducting experimental studies, the following reagents were used: thiophene (Biochem Chemopharma, ≥99.0%), *n*-hexane (HIMMED, qualification chemically pure), polyethylene glycol 400 (Clariant), polypropylene glycol 425 (Acros Organics), polyvinylpyrrolidone 3500 (Acros Organics, ≥99%), sodium nitrate (HIMMED, qualified chemically pure), and 1-methyl-2-pyrrolidone (Acros Organics, 99%). All reagents were used without further purification.

Stock solution, modeling light hydrocarbon fractions, was prepared by dissolving thiophene with a concentration of 0.05 wt % in *n*-hexane. The extractant solution was prepared by dissolving an exact

weighed portion of a hydrophilic polymer, sodium nitrate and 1-methyl-2-pyrrolidone, suspended on an analytical balance (OHAUS Explorer) in distilled water.

To study the thiophene extraction process, graduated plastic tubes and dividing funnels with ground stoppers were used. The extraction was carried out by mixing equal volumes of an aqueous solution of an extractant and a solution of thiophene in *n*-hexane; then the resulting mixture was stirred in an EnvironGenie thermostatic shaker (Scientific Industries, Inc.) at a temperature of 25°C at a rotation speed of 45 rpm for 1 h to achieve the thermodynamic equilibrium of the system. The mixture was then centrifuged for 10 min at 2500 rpm (centrifuge CM-6MT, SIA ELMI), after which the phase volumes were measured. The concentration of thiophene in the organic phase was determined spectrophotometrically (spectrophotometer Cary-60, Agilent) at a wavelength of 228 nm in quartz cuvettes with an optical path length of 1 mm relative to *n*-hexane. The thiophene concentration in the aqueous phase was determined by the difference between its concentration in the initial solution and in the organic phase after extraction.

The degree of extraction of thiophene E was calculated by the formula

$$E = \frac{C_{\text{bot}}^{\text{T}} V_{\text{bot}}}{C_{\text{top}}^{\text{T}} V_{\text{top}} + C_{\text{bot}}^{\text{T}} V_{\text{bot}}} \times 100\%,$$

where $C_{\text{bot}}^{\text{T}}$ is the molar concentration of thiophene in the bottom phase, mol/L; $C_{\text{top}}^{\text{T}}$ is the molar concentration of thiophene in the top phase, mol/L; and $V_{\text{bot}}, V_{\text{top}}$ are volumes of the top and bottom phases, respectively, mL.

RESULTS AND DISCUSSION

The effect of introducing individual and multicomponent additives 1-methyl-2-pyrrolidone, sodium nitrate, and water-soluble polymers (polyethylene glycol 400, polypropylene glycol 425, and polyvinylpyrrolidone 3500) into the model *n*-hexane–water system on the efficiency of extracting thiophene in the aqueous phase has been experimentally studied.

The dependences of the efficiency of extracting thiophene from *n*-hexane in water by adding 1-methyl-2-pyrrolidone to the system were found. Figure 1 shows the dependence of the degree of extraction of thiophene from *n*-hexane ($\omega_{\text{(in)}} = 0.05$ wt %) of the content of 1-methyl-2-pyrrolidone with a volume ratio of aqueous and organic phases of 1 : 1. It was found that, with an increase in the content of 1-methyl-2-pyrrolidone in the *n*-hexane–water system, there is an exponential increase in the degree of extraction of thiophene. The use of pure 1-methyl-2-pyrrolidone results in the recovery of thiophene from

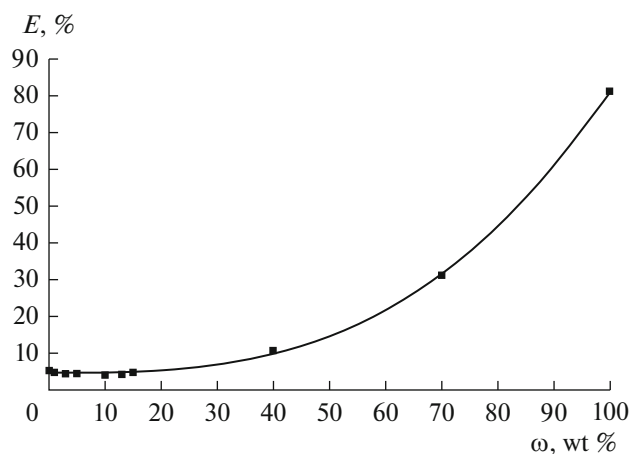


Fig. 1. Dependence of the degree of extraction of thiophene on the concentration of 1-methyl-2-pyrrolidone in the *n*-hexane–water system (volumetric ratio of phases 1 : 1).

n-hexane by 81% for one extraction step, which fully agrees with the data of other authors [9–11].

Figure 2 shows the dependence of the degree of extraction of thiophene from *n*-hexane from sodium nitrate under similar conditions. As you can see, the introduction of sodium nitrate into the system and an increase in its concentration up to 40 wt % leads to an increase in the efficiency of the extraction of thiophene in the salt phase by 2 times.

The next stage of research was the study of the extraction behavior of thiophene in the *n*-hexane–water system when two-component additives were administered: polymer and inorganic salt. The polymer content was constant and amounted to 15 wt %. With this polymer content, the influence of additional reagents manifests itself most vividly and provides the maximum possible range for varying the amounts of additives introduced into the extraction system. Earlier in [21], the values of the degree of extraction of thiophene in the *n*-hexane–water system with the introduction of 15 wt % water-soluble polymer were established (Table 1).

The highest value of the degree of extraction of thiophene is observed with the introduction of polyvinylpyrrolidone 3500, which can be explained by the presence of the pyrrolidone ring in the polymer structure, due to which the π – π interaction with the thiophene ring is formed. As a result of this, thiophene is easily polarized and, due to the presence of discrete π bonds, passes into a polar solvent.

Figure 3 presents the results of an experimental study of the impact of coadministration in the *n*-hexane–water system of 15 wt % water-soluble polymer (PEG-400, PPG-425, PVP-3500) and sodium nitrate in the concentration range from 0 to 20 wt % on the degree of extraction of thiophene with a 1 : 1 phase volume ratio. The experimental data show that the

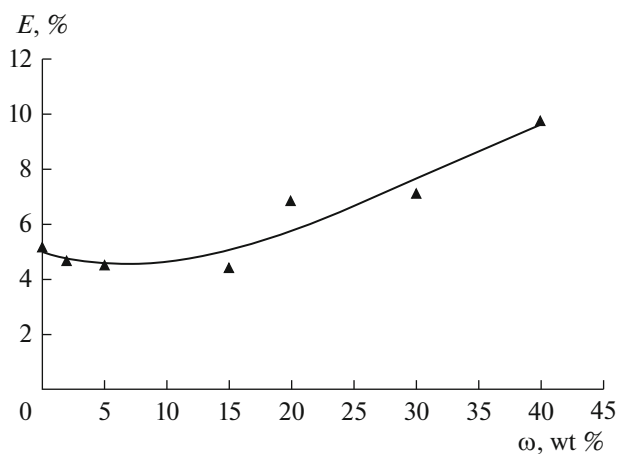


Fig. 2. Dependence of the degree of extraction of thiophene on the concentration of sodium nitrate in the *n*-hexane–water system (volumetric ratio of phases 1 : 1).

introduction of PEG-400 (or PPG-425) and sodium nitrate allows the more efficient extraction of thiophene compared to systems in the absence of sodium nitrate [21], while the introduction of PVP-3500 and sodium nitrate into the system, on the contrary, leads to a significant deterioration in extraction: the degree of extraction is reduced 3 times. The greatest effect of the combined introduction of the polymer and salt has a system based on PEG-400 and sodium nitrate, which allows you to increase the efficiency of extraction of thiophene by 7 times. When polypropylene glycol 425 is introduced into the system, a slight increase in the degree of extraction of thiophene is observed. It should be noted that an increase in the concentration of sodium nitrate to 10 wt % or more does not lead to a significant change in the degree of extraction of thiophene.

Similar dependences of the efficiency of thiophene extraction on the content of the introduced component were obtained for the water-soluble polymer (PEG-400, PPG-425, and PVP-3500) and 1-methyl-2-pyrrolidone mixture (Fig. 4). For the studied polymers with the introduction of 1-methyl-2-pyrrolidone, the same trends are observed as with the introduction of sodium nitrate. The simultaneous administration of PEG-400 and 1-methyl-2-pyrrolidone increases the extractability of thiophene from 3 to 22%; the use of PPG-425 and 1-methyl-2-pyrroli-

Table 1. Thiophene extraction levels in the *n*-hexane–water system with the introduction of 15 wt % water soluble polymer [21]

Polymer	E, %
Polyethylene glycol 400	3.32
Polypropylene glycol 425	12.67
Polyvinylpyrrolidone 3500	14.91

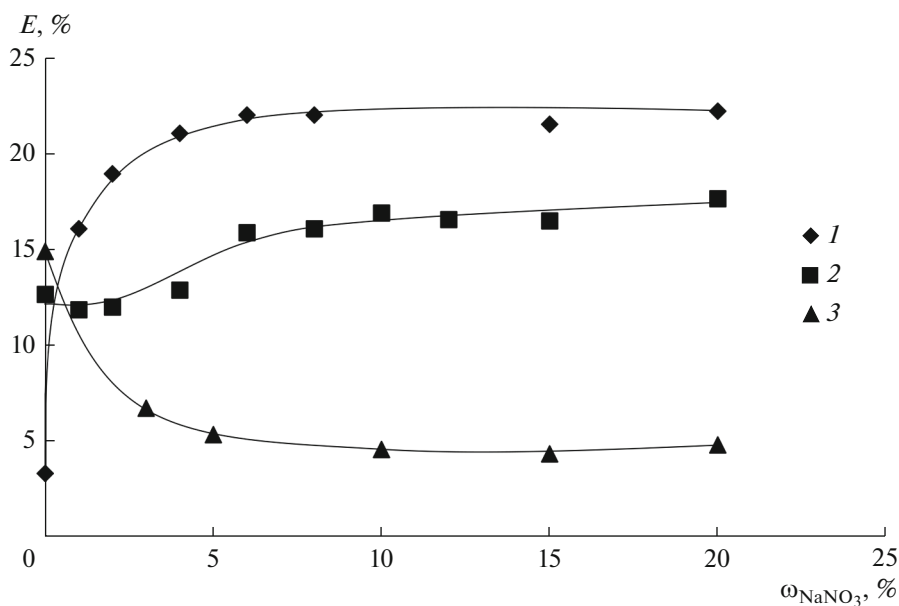


Fig. 3. Impact of introducing into the *n*-hexane–water system a mixture of sodium nitrate and PEG-400 (1), PPG-425 (2), and PVP-3500 (3) on the degree of extraction of thiophene.

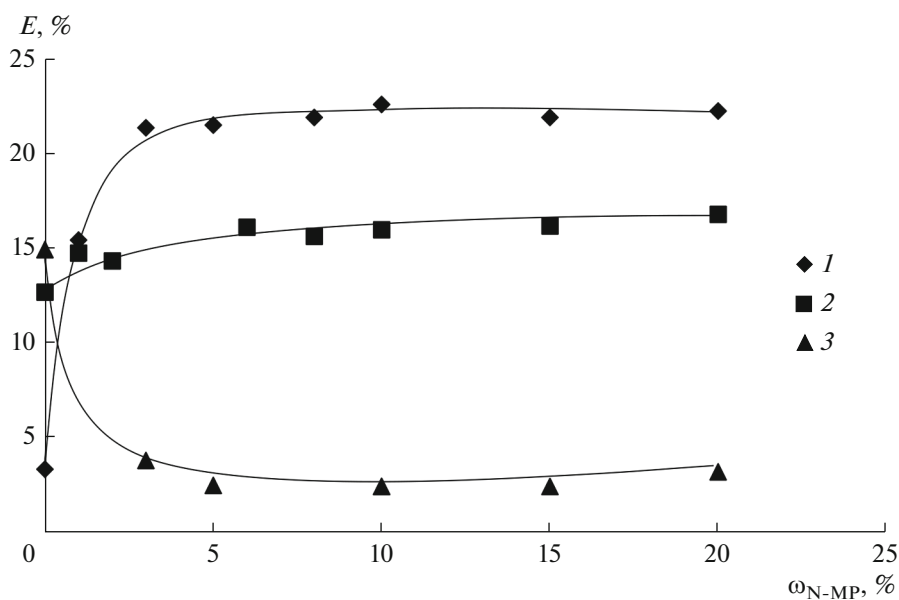


Fig. 4. Impact of introducing into the *n*-hexane–water system a mixture of 1-methyl-2-pyrrolidone and PEG-400 (1), PPG-425 (2), and PVP-3500 (3) on the degree of extraction of thiophene.

done weakly affects the extractability of thiophene, increasing it by only 3% [21]; and the introduction of PVP-3500 and 1-methyl-2-pyrrolidone reduces the extraction efficiency from 15 to 3%.

The analysis of dependences presented in Figs. 1–4 shows that the nature of the polymer plays a decisive role in the extraction of thiophene. Introducing polyethylene glycol 400 to the extraction *n*-hexane–water system leads to a significant increase in the degree of extraction of thiophene both in the presence of

sodium nitrate and 1-methyl-2-pyrrolidone when compared with additive values. When thiophene is extracted in the presence of polypropylene glycol 425, the degree of extraction is comparable to the additive value. The introduction of polyvinylpyrrolidone 3500, on the contrary, leads to a significant decrease in the extraction efficiency.

The effect of cointroducing into the *n*-hexane–water system a three-component mixture of a water-soluble polymer, sodium nitrate and 1-methyl-2-pyr-

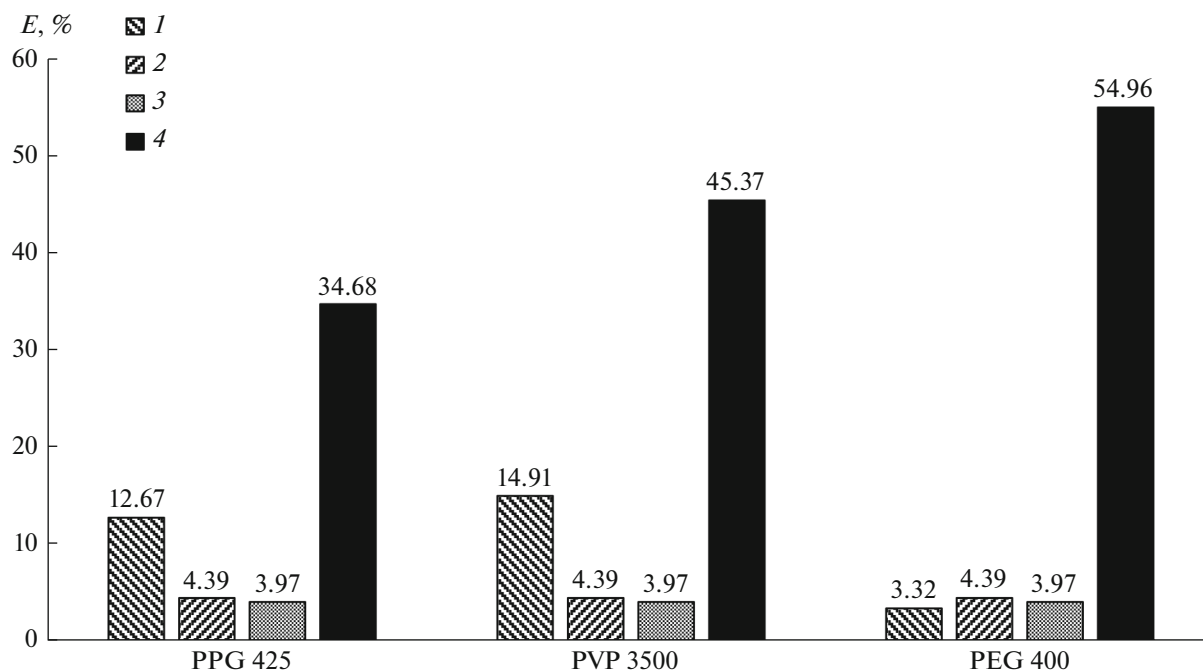


Fig. 5. Degree of extraction of thiophene from *n*-hexane with the introduction of 15 wt % polymer (1); 10 wt % sodium nitrate (2); 5 wt % 1-methyl-2-pyrrolidone; (3) and mixtures polymer (15 wt %), sodium nitrate (10 wt %), and 1-methyl-2-pyrrolidone (4).

rolidone, on the degree of extraction of thiophene is investigated. The results are shown in Fig. 5. The data show that the simultaneous administration of 15 wt % polymer (PEG-400, PPG-425, and PVP-3500), 10 wt % sodium nitrate, and 5 wt % 1-methyl-2-pyrrolidone lead to a significant increase in the degree of extraction of thiophene when compared with the additive value, with the greatest positive effect observed with the introduction of polyethylene glycol 400.

CONCLUSIONS

A series of systematic studies of the effect of individual and multicomponent additives—polyethylene glycol 400, polypropylene glycol 425, polyvinylpyrrolidone 3500, sodium nitrate, and 1-methyl-2-pyrrolidone—on the extraction of thiophene in an *n*-hexane–water system was carried out. It was found that the introduction of a small amounts of additives in the aqueous phase leads to a significant increase in the degree of extraction of thiophene from *n*-hexane in the aqueous phase in comparison with the individual components. The study opened up new possibilities for controlling the efficiency of the process of extracting thiophene from light hydrocarbon fractions, which is of great practical importance. Further research in this direction will focus on optimizing the conditions for extracting sulfur-containing components from light hydrocarbon fractions using promising environmentally friendly systems based on water-soluble polymers (polyethylene glycol 400, etc.) in order to increase efficiency.

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NOTATION

C	concentration, mol/L
E	degree of extraction, %
V	volume, mL
ω	concentration, wt %

SUBSCRIPTS AND SUPERSSCRIPTS

top	top phase
in	initial value
bot	bottom phase

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