Thiophene extraction in PEG - hexan - water based systems

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Abstract. The effect of individual and multicomponent additives of sodium chloride, iron chloride, sodium nitrate and 1-methyl-2-pyrrolidone on the interfacial distribution of thiophene in the systems polyethylene glycol 1500 (PEG-1500) - hexane - water and polyethylene glycol 8000 (PEG-8000) - hexane - water has been studied in this investigation. It was found that in most cases, the introduction of a small amount of individual and joint additives increases the extraction of thiophene from the organic phase to the aqueous.

Key words: liquid – liquid equilibrium, interphase distribution, thiophene, water soluble polymers, inorganic salts, n-hexane, light hydrocarbon fractions.

1. Introduction
Light hydrocarbon fractions obtained during oil refining contain a large number of sulfur-containing compounds [1]. Sulfur oxides are released into the atmospheric air, which negatively affect the environment [2] and human health [3] during the combustion of such fractions. Recently, increasingly stringent environmental requirements for sulfur content have been imposed on the quality of light fractions [4]. The traditional method for removing sulfur compounds from light hydrocarbon fractions is hydrotreating [2], sorption [5], oxidation [3], and extraction [6, 7]. Liquid-liquid extraction is a priority in comparison with other traditional methods of separating multicomponent mixtures, for example, rectification, which is energy-intensive [8, 9]. For example, extraction is used to isolate, separate, and concentrate both acids [10] using binary extractants [11, 12] and metals [13]. Extraction is also used in other studies, for example, in chromatography [14,15] or in supercritical fluid technologies [16, 17]. Recently, extraction methods of purification of light hydrocarbon fractions from sulfur-containing compounds have become especially relevant [18]. In the process of desulfurization of light hydrocarbon fractions, traditional extractants such as DMSO, DMF, acetonitrile, sulfolane and others are toxic, fire hazardous and environmentally unsafe [19]. Alternatively, extraction systems based on water-soluble polymers are used [20], so Voshkin et al. Studied the extraction of benzoic, salicylic, and sulfosalicylic acids in a two-phase aqueous system PEG-1500 - sodium sulfate - water [21], Zakhodyaeva et al. Studied the liquid-liquid equilibrium of the two-phase system PEG-1500 - sodium nitrate - water at three different temperatures and plotted phase diagrams [22], these systems are also used in the extraction of metals [23, 24], and also Gradov et al. Investigated the distribution of iron (III) ions in two-phase aqueous systems in the presence of ultrasound [25]. Such systems are a priority in comparison with classical water – organic solvent extraction systems, since these systems are non-toxic, fire-safe, cheap and easy to use [26], for example, these systems were used by Zinoviev et al. To study the distribution of caffeine and coumarin [27]; they also studied the extraction of monocarboxylic acids from dilute
solutions using extraction systems based on polyethylene glycols with different molecular weights [28]. Zakhodyaeva et al. Studied the liquid-liquid equilibrium of a non-toxic and fire-safe two-phase water system, consisting of polyvinylpyrrolidone 3500 and sodium nitrate, and also mentioned that this system is promising in the process of extracting polycyclic sulfur-containing compounds from light hydrocarbon fractions [29]. In work [30] Zakhodyaeva et al. Investigated the extraction separation of non-ferrous metals from leaching solutions of active elements of batteries using a two-phase water system PEG-1500 - ammonium sulfate - water.

The aim of this work was to study the effect of individual and multicomponent additives in the systems PEG-1500 - hexane - water and PEG-8000 - hexane - water on the degree of extraction of thiophene from n-hexane in the polymer phase.

2. Experimental details

2.1. Reagents

The following reagents were used in experimental studies: thiophene (Biochem Chemopharma, ≥ 99.0%), n-hexane (CHEMMED, «c.p.»), polyethylene glycol 1500 (Fluka), polyethylene glycol 8000 (Fluka), sodium chloride (CHEMMED, «p»), iron (III) chloride (CHEMMED, «c.p.»), sodium nitrate (CHEMMED, «c.p.»), 1-methyl-2-pyrrolidone (Acros Organics, 99%).

2.1.1. Research methods

The initial solution simulating 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 suspension of a hydrophilic polymer and an injectable additive suspended on an analytical balance (OHAUS Explorer) in distilled water.

To study the thiophene extraction process, graduated tubes and dividing funnels with ground stoppers were used. The extraction was carried out by mixing equal volumes of an aqueous solution of the extractant and a solution of thiophene in n-hexane, then the resulting mixture was mixed in an Enviro-Genie temperature-controlled shaker (Scientific Industries, Inc.) at a temperature of 25 °C at a rotation speed of 45 rpm for 1 hour for achieving thermodynamic equilibrium of the system. The mixture was then centrifuged for 10 min at 2500 rpm (centrifuge CM-6MT, SIA ELM), 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. 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.

3. Results and discussion

During the experimental work, the influence of individual and joint additives on the degree of interphase distribution of thiophene in the PEG-1500 – hexane – water and PEG-8000 – hexane – water systems was studied.

Previously, we experimentally found that the introduction of individual additives of more than 10% sodium nitrate, 5% 1-methyl-2-pyrrolidone, 2% ferric chloride in the hexane - water system are optimal and a further increase in the concentration of reagents does not lead to an increase in the degree of extraction of thiophene. Consequently, the concentrations of substances in multicomponent additives are the same as individual ones.

In fig. 1-2 show the results of the dependence of the extraction efficiency on the content of various additives in the polymer-hexane-water systems.

As can be seen from the presented fig. 1, multicomponent additives (2% iron (III) chloride + 10% sodium nitrate and 10% sodium nitrate + 5% 1-methyl-2-pyrrolidone) exhibit effective extraction properties in comparison with individual ones. This is due to the combined effect of the additives on the
extraction of thiophene from hexane. Also their rice. 1 that the addition of 10% sodium nitrate to the PEG-1500 - hexane - water system results in 25% recovery of thiophene from hexane.

The obtained experimental data (Fig. 2) show that the introduction of multicomponent additives has practically no effect on the efficiency of thiophene extraction in comparison with the PEG-8000 - hexane - water system. It is also seen from the obtained data that the introduction of 10% sodium nitrate leads to almost the same value of extraction efficiency as in the case of the PEG-1500 – hexane – water system.

![Figure 1](image_url)

**Figure 1.** The dependence of the degree of thiophene extraction on the content of various additives in the PEG-1500 – hexane – water system.
Comparing Fig. 1 and 2, it can be seen that with the addition of 2% ferric chloride, 10% sodium nitrate and 5% 1-methyl-2-pyrrolidone to the extraction system, the efficiency of thiophene extraction is practically the same for PEG-1500-hexane-water and PEG-8000-hexane-water. It is also seen that sodium chloride as an additive does not exhibit effective extraction properties and practically does not extract thiophene from the organic phase. However, the addition of multicomponent additives to the PEG-1500-hexane-water system exhibits more effective properties in the process of extracting thiophene from hexane, compared to their addition to the PEG-8000-hexane-water system.

4. Conclusions
The study conducted a series of systematic studies of the dependence of the degree of thiophene extraction on the content of various additives, in particular, sodium chloride, iron (III) chloride, sodium nitrate and 1-methyl-2-pyrrolidone in the PEG-1500-hexane-water and PEG-8000-hexane-water systems. It was found that individual and multicomponent introduction of additives into systems in most cases increases the degree of thiophene extraction from n-hexane to the polymer phase. As a result, there is a need for further research to increase the efficiency of these systems in the processes of purification of light hydrocarbon fractions from sulfur containing compounds.

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