Extraction of pyridine using systems based on water-soluble polymers

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Abstract. In the process of using hydrocarbon fractions containing a large amount of nitrogenous compounds, nitrogen oxides are released into the atmospheric air, which have a negative impact on the environment and human health. The traditional cleaning method is treatment with a 25% sulfuric acid solution and subsequent hydrotreating. However, this process becomes disadvantageous due to its inability to achieve ultra-low concentrations of nitrogen-containing compounds (<10 ppm). Extraction using non-toxic and environmentally friendly water-soluble polymers is a promising alternative compared to traditional methods. This work presents the dependence of the interphase distribution of pyridine on the composition of extraction systems based on water-soluble polymers. According to the results of the study, it was found that polyethylene glycol-400, polypropylene glycol-425 and methyl ether of polyethylene glycol-350 exhibit effective extraction properties in relation to pyridine and extract it by 90.95%, 90.33% and 87.82% in one extraction stage, respectively. It was also found that the use of two-phase aqueous systems based on water-soluble polymers in the process of extracting pyridine is promising.

Keywords: green chemistry, liquid–liquid extraction, extraction efficiency, interphase distribution, pyridine, water soluble polymers, light hydrocarbon fractions.

1. Introduction
Light hydrocarbon fractions are the most important product of the oil refining industry. Also, in the process of using such fractions, nitrogen oxides are released into the atmospheric air, which negatively affect the environment and human health [1]. The quality of the yield of light fractions is subject to stringent requirements for the content of nitrogen compounds, since at the stage of processing petroleum feedstock they significantly reduce the activity of catalysts, cause tar formation and darkening of petroleum products [2]. All nitrogen-containing compounds in the oil are divided into three groups, the largest of which is the group of basic heterocycles, the share of such compounds in oils is up to 60% of the total nitrogen content [3]. The traditional method for removing nitrogen-containing compounds is treatment with a 25% sulfuric acid solution and subsequent hydrogenation [4]. However, obtaining fractions of the desired quality with a low content of nitrogen compounds (<10 ppm) becomes economically unprofitable [5]. As a consequence of this, recently, alternative methods for the isolation and concentration of nitrogen-containing compounds have been developed, such as oxidation [6], sorption [7], and extraction [8]. Extraction is a priority in comparison with other separation methods since in most cases it proceeds under normal conditions (T = 25°C, atmospheric pressure), does not require complex instrumentation and does not change the chemical structure of compounds and, therefore, does not affect the quality of liquid fuel [9, 10]. Liquid-liquid extraction is applicable in the processes of isolation, separation, and concentration of a number of carboxylic acids [11, 12], non-ferrous [13, 14], and rare earth metals [15-17]. Extraction is applicable in other areas of technology such as chromatography [18, 19], pseudo-liquid membranes [20], and supercritical fluids [21]. Traditional organic solvents used as extractants in the processes of removing nitrogen compounds from fuels, for example, dimethylformamide [22], are toxic and fire hazardous. Systems based on water-soluble polymers are used as an alternative [23]. The advantage of these systems is their non-toxicity and environmental safety [24]. The applicability of these
systems in the extraction of carboxylic acids has been described by Zinovieva et al. [25]. The authors of the article [25] studied the dependences of the interphase distribution of benzoic, salicylic, and sulfosalicylic acids on the composition of two-phase aqueous systems, temperature, and pH values. Many researchers have studied the extraction of metals, so the article [26] studied the extraction of iron (III) chloride in a two-phase aqueous system polypropylene glycol 425 - sodium chloride - water. The authors of the article [27] in their work present an ecologically safe aqueous two-phase system based on polyethylene oxide for the complex extraction of Ni (II), Co (II), Fe (III), Mn (II), Zn (II), Cu (II) and Al (III) from nitrate solutions, in this article we studied the effect of various parameters of the system on the extraction behavior, such as the acidity of the medium, temperature, initial metal concentration and contact time of the phases. Oscherel, Gradov, et al. Studied the effect of ultrasonic radiation on the extraction of Fe^{3+} ions from chloride and nitrate solutions in systems based on water-soluble polymers [28]. Previously, we studied the interphase distribution of thiophene in systems based on water-soluble polymers, and it was found that the system based on polyethylene glycol 400 exhibits effective extraction properties with respect to thiophene. [29] Also, systems based on water-soluble polymers are used in the processes of removing nitrogen-containing compounds from petroleum products, so Jiang et al. [30] investigated the dependence of the extraction of basic and non-basic nitrogen-containing compounds on the composition of systems based on water-soluble polymers. Zhu et al. [31] proved the effectiveness of the use of deep eutectic solvents based on water-soluble polymers in the processes of fuel purification from nitrogen-containing compounds.

As a result, in the processes of purification of light hydrocarbon fractions, extraction systems that correspond to the principles of "green" chemistry are of particular relevance, and the purpose of this work was to study the interphase distribution of pyridine in two-phase systems polymer - n-hexane - water.

2. Experimental details

2.1. Reagents

The following reagents were used in experimental studies: pyridine (CHIMMED), n-hexane (CHIMMED), polyethylene glycol 400 (Clariant), polypropylene glycol 425 (Acros Organics), polyethylene glycol methyl ether 350 (Acros Organics). All reagents were used without additional purification.

2.2 Research methods

An initial solution simulating light hydrocarbon fractions, a ready-made pyridine solution with a concentration of 0.05% (wt.) in n-hexane.

To study the process of pyridine extraction, we used graduated test tubes and separating funnels with ground stoppers. Extraction of solutions simulating hydrocarbon fractions, solutions of an extractant based on a water-soluble polymer. Next, the resulting mixture was stirred for 1 hour in a thermostated shaker Enviro-Genie (Scientific Industries, Inc.) at a temperature of 25°C and at a speed of 45 rpm to achieve thermodynamic equilibrium of the system. Then the mixture was centrifuged for 10 min at 2500 rpm (centrifuge CM-6MT, SIA ELMI), after which the volumes of the phases were measured. The concentration of pyridine in the organic phase was determined spectrophotometrically (spectrophotometer Cary-60, Agilent) at a wavelength of 251 nm (for this, the electronic absorption spectrum in the ultraviolet region was captured, fig. 1) in quartz cells with an optical path length of 1 mm relative to a solution in which pyridine is dissolved.
For the quantitative determination of pyridine, a calibration straight line (Fig. 2) was constructed at five points, at the corresponding wavelength of 251 nm and $R^2$ was 0.9994.

**3. Results and discussion**

In the course of the experimental work, the interfacial distribution of pyridine was studied in the systems polyethylene glycol 400 - n-hexane - water, polypropylene glycol 425 - n-hexane - water, and polyethylene glycol methyl ether 350 - n-hexane - water.

In fig. 3 shows the results of the dependence of the degree of extraction of pyridine from n-hexane on the composition of extraction systems based on water-soluble polymers.
As can be seen, extraction systems based on polyethylene glycol 400, polypropylene glycol 425, and polyethylene glycol methyl ether 350 have high selectivity with respect to pyridine, extracting it up to 90.95%, 90.33% and 87.82% in one extraction stage, respectively. It should be noted that the use of 100% polypropylene glycol 425 is excluded since this leads to the formation of a homogeneous system and the process of extracting pyridine from n-hexane, in this case, becomes impossible. Therefore, the use of an aqueous solution of polypropylene glycol 425 makes it possible to implement the pyridine extraction process. Also, from fig. 3 it can be seen that systems containing 90% and 95% have practically the same efficiency, extracting pyridine from n-hexane by 90.22% and 90.33% for one degree of extraction, respectively.

4. Conclusions
Within the framework of this work, a series of systematic studies of the dependence of the degree of extraction of pyridine from n-hexane on the composition of extraction systems based on water-soluble polymers was carried out. It was found that polyethylene glycol 400, polypropylene glycol 425 and polyethylene glycol methyl ether 350 exhibit effective extraction abilities with respect to pyridine and extract it by 90.95%, 90.33% and 87.82% in one extraction stage, respectively. Based on the results of this study, there is a need for further research to improve these systems in order to increase the efficiency of extracting nitrogen compounds from light hydrocarbon fractions.

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