Interphase distribution of a number of polybasic carboxylic acids in aqueous two-phase systems based on polyethylene glycol-1500.

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Abstract. In this work, we studied the interphase distribution of a number of polybasic carboxylic acids, in particular, malic, succinic, glutaric, citric, ascorbic and tartaric in two-phase aqueous systems polyethylene glycol-1500 (PEG-1500) - sodium sulfate - water and PEG-1500 - ammonium sulfate - water. Using the spectrophotometric method of analysis, quantitative characteristics (interfacial distribution and degree of recovery) of the extraction of carboxylic acids were determined. In conclusion, it was found that the considered two-phase aqueous systems are promising in the process of extraction of polybasic carboxylic acids. In particular, the system polyethylene glycol 1500 - sodium sulfate - water has effective extraction properties for succinic malic and ascorbic acids. On the other hand, depending on the composition of the extraction systems, the quantitative characteristics for citric, glutaric and tartaric acids practically do not differ.

Key words: green chemistry, liquid extraction, aqueous two-phase systems, extraction degree, interphase distribution, polyethylene glycol 1500, sodium sulfate, ammonium sulfate, carboxylic acids.

1. Introduction
The development and implementation of «green» extraction systems to solve problems associated with the purification, concentration and separation of mixtures is one of the rapidly developing areas in chemical technology [1, 2]. Thus Egorova et al investigated the extraction of lanthanides using binary extractants [3]. In work Zakhodyaeva the extraction separation of non-ferrous metals from leaching solutions of active elements of batteries was studied [4]. In investigate Voshkin studied the extraction of iron (III) ions using binary extractants [5]. Aqueous two-phase systems are environmentally friendly, non-toxic, cheap and easy to use, in comparison with classical extraction systems [6, 7]. Voshkin et al. investigated the interphase distribution of aromatic acids in a two-phase aqueous system polyethylene glycol – sodium sulfate – water [8]. The authors of the work [9] studied the extraction of thiophene, o-xylene, and toluene in hexane – polymer – water systems. In work Zinov’eva the interfacial distribution of caffeine and coumarin in a system based on polyethylene glycol and sodium sulfate was considered [10]. Zakhodyaeva et al. developed phase diagrams of two-phase aqueous systems polyethylene glycol 1500 – nitrate nitrate – water and polyvinylpyrrolidone 3500 – sodium nitrate – water at three different temperatures [11, 12]. Such systems have found their
application in extraction technologies for the purification and separation of organic and inorganic substances [13, 14]. Zinovyeva et al. studied the extraction of benzoic, salicylic, and sulfosalicylic acids using two-phase aqueous systems based on polyethylene glycol [15]. In work Chen, the authors investigated the selective separation of neodymium (III) and samarium (III) in two-phase systems [16]. The authors of the work [17] studied the extraction of metal ions in two-phase aqueous systems based on polyethylene glycol and sodium sulfate. Tong et al. investigated the extraction of platinum from hydrochloric acid solutions using two-phase systems [18]. Also, in the processes of acid extraction, both binary extractants [19-21] and neutral [22, 23] are used. In addition to traditional liquid-liquid extraction, there are also liquid-liquid chromatographic separation of substances [24, 25], as well as supercritical fluid technologies [26, 27].

These systems can also be used in the extraction of carboxylic acids [13, 15]. Polybasic carboxylic acids, such as malic, succinic, glutaric, citric, ascorbic and tartaric acids are widely used in various fields of various industries, such as food, pharmaceutical, cosmetic, etc., as food additives, organic fertilizers, in the preparation of medicines, in the synthesis of polyamides, in the production of 1,5-pentanediol. Polybasic carboxylic acids are found in natural or man-made products, for example, in water-acid effluents of caprolactam production [28, 29]. So Jazz et al. investigated the extraction of carboxylic acids from organic solvents using supercritical fluid technologies [30]. As a result, there is a need to allocate carboxylic acids of technogenic water runoff.

The aim of this work is to study the interphase distribution of a number of carboxylic acids, in particular malic, succinic, glutaric, citric, ascorbic and tartaric acids, in two-phase aqueous systems PEG-1500 - sodium sulfate - water and PEG-1500 - ammonium sulfate - water during the extraction of a number polybasic carboxylic acids.

### 2. Experimental details

#### 2.1. Reagents

The following reagents were used in experimental studies: polyethylene glycol 1500 (PEG-1500) (Fluka), sodium sulphate («c.p.»), ammonium sulphate («c.p.»), malic acid (CHEMMED, «p»), succinic acid (CHEMMED, «p»), glutaric acid (CHEMMED, «p»), citric acid (CHEMMED, «c.p.»), ascorbic acid (CHEMMED, «c.p.»), tartaric acid (CHEMMED, «p.a.»). All reagents were used without further purification.

#### 2.2. Research methods

The initial solutions of polybasic carboxylic acids were prepared by dissolving precise attachments suspended on analytical scales in distilled water.

To study the process of extraction of carboxylic acids in aqueous two-phase systems, graduated test tubes and dividing funnels with sanded stoppers were used. For this, exact weighed portions of a water-soluble polymer and a phase-forming salt, weighed on an analytical balance (OHAUS Explorer), were placed in a test tube and dissolved in aqueous solutions of carboxylic acids, then the resulting mixtures were mixed for 30 minutes. at a rotation speed of 45 rpm in an Enviro-Genie thermostatic shaker (Scientific Industries, Inc.) at 25 °C to achieve thermodynamic equilibrium. The mixture was then centrifuged for 5 minutes. at 2500 rpm (centrifuge CM-6MT, SIA ELM), after which phase volumes were measured.

Quantitative characteristics of the extraction process were determined by spectrophotometric analysis (Cary-60, Agilent spectrophotometer). For the quantitative determination of malic, succinic, glutaric, citric, ascorbic and tartaric acids, calibration lines were constructed at five points, with wavelengths of 205, 201, 203, 206, 244 and 210 nm, respectively, and R² was 0.9998, 0.9996, 0.9986, 0.9989, 0.9999, 0.9999, respectively. The wavelength data for each of the acids were determined experimentally using a spectrophotometric analysis method.
3. Results and discussion

During the experimental work, the interphase distribution of malic, succinic, glutaric, citric, ascorbic and tartaric acids in aqueous two-phase systems PEG – 1500 – sodium sulfate-water and PEG – 1500 – ammonium sulfate-water was studied.

Fig. 1-2 shows experimental results of the distribution coefficient of the considered polybasic carboxylic acids in aqueous two-phase systems PEG-1500-sodium sulfate-water and PEG-1500-ammonium sulfate-water. These systems also exhibit effective extraction properties with respect to multi-base carboxylic acids in comparison with traditional organic extractants. According to these figures, the distribution coefficient for citric, ascorbic, glutaric and tartaric acids practically does not differ depending on the composition of the aqueous two-phase system. However, the PEG-1500-sodium sulfate-aqueous system shows more pronounced extraction properties in relation to succinic and malic acids, compared to the PEG-1500 – ammonium sulfate – aqueous system. As a result, there is a need for further research to increase the efficiency of these systems in the extraction of polybasic carboxylic acids. Determine the equilibrium time a series of experiments on varying the phase contact time from 3 to 60 minutes Figure 1 were carried out. As can be seen from Figure 1 a slight increase in the Ce(III) distribution coefficient over the studied time interval is observed. In case of La(III) an increase in the distribution coefficient is observed up to 20 minutes and then it decreases, which may be due to the emulsification effect.

![Figure 1](image)

**Figure 1.** Distribution coefficients polybasic carboxylic acids in aqueous two-phase system PEG-1500-sodium sulfate-water, where $D$ is the distribution coefficient.
Figure 2. Distribution coefficients polybasic carboxylic acids in aqueous two-phase system PEG-1500-ammonium sulfate-water, where D is the distribution coefficient.

Comparing the results obtained in figure 1 and 2 show that the PEG-1500 - sodium sulfate - water system has more pronounced extraction properties in relation to succinic malic and ascorbic acids. On the other hand, depending on the composition of the extraction system, the quantitative characteristics for citric, glutaric and tartaric acids practically do not differ.

4. Conclusions
A series of systematic studies of the interfacial distribution of a number of polybasic carboxylic acids in aqueous two-phase systems of different composition was carried out. During the study, it was found that the systems PEG-1500-sodium sulfate-water and PEG-1500-ammonium sulfate-water exhibit effective extraction properties in relation to the considered polybasic carboxylic acids in comparison with traditional organic extractants. The use of two-phase aqueous systems in the extraction of polybasic carboxylic acids is promising in view of their non-toxicity, fire safety, and low cost in comparison with traditional organic extractants. Research will also continue to improve these systems in order to increase the efficiency of extraction of polybasic carboxylic acids.

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Acknowledgement
The reported study was funded by RFBR according to the research project № 18-29-06070