The possibility of using DES based on polypropylene glycol 425 and tetrabuthylammonium bromide in the extraction processes of transition metals

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Abstract. Traditionally, the method of liquid extraction is used to extract metals from aqueous. This work is devoted to the combination of perspective alternative for hazardous solvents (aqueous two-phase systems based on water-soluble polymers) and the novel deep eutectic solvents in the non-ferrous metals extraction processes. In this work, the synthesis of deep eutectic solvent based on a water-soluble polymer (PPG-425) and tetrabutylammonium bromide (TBAB) by stirring for 10 minutes at 80°C has been shown. The obtained results showed not only the possibility of using DES in the metal extraction process, but the selectivity to the Fe(III) and Zn(III), the distribution coefficients were 71.64 and 25.17 respectively. The metal concentrations were determined spectrophotometrically using 4-(2-pyridylazo)resorcinol. This work shows the perspectives of using DESs in the metal extraction processes.

Key words: liquid-liquid extraction, aqueous two-phase systems, deep eutectic solvents, «green» chemistry

1. Introduction
In recent years, much attention has been paid to the transition from traditional methods of extraction and separation of various metals from discharged lithium-ion batteries to methods that take into account the principles of «green» chemistry [1]. The traditional methods involved the using of various solvents and substances that were harmful to the environment and health [2]. At the beginning of the twenty-first century, deep eutectic solvents (DESs) were developed, they became promising alternative for hazardous organic solvents. DESs are systems formed from a eutectic mixture of Lewis and Bronsted acids and bases, which may contain various anionic and/or cationic substances. One of the DESs components should act as a hydrogen bond donor, and the other as an acceptor, as a result of which they form a eutectic mixture with a melting point much lower than the melting temperature of any of the individual components [3]. At present DESs have found applications in different fields of chemistry. They are used in biotechnological processes, for example, for the separation of RNA [4], for the electrodeposition of metals [5], for the extraction or metal compounds from aqueous media [6], in analytical chemistry [7], for the synthesis of iron [8] or zinc [9] nanoparticles.

In addition to the principles of «green» chemistry, researchers began to worry about the problems of the limited non-renewable resources of the Earth, including various metals, the mining and processing
of which is a source of environmental pollution. Electronic waste is a huge problem, because if it is not recycled, then the heavy metals that are contained in them are released into the environment. Their processing involves the use of strong acids at the leaching stage, and the following extraction of metals from the resulting leach solutions in water-organic solvent systems, which does not comply with the principles of «green» chemistry and are toxic, flammable and explosive [10,11]. One of the most common methods for the extraction of organic and inorganic substances is liquid extraction by the systems based on water and organic solvent. At present, hybrid methods of liquid-liquid chromatography are known, which are the most effective in comparison with traditional extraction using mixing and settling apparatus. Counter-current chromatography [12,13,14] is of the greatest interest, since its use implies not only an analytical aspect, but also a preparative one, that is, application in order to extract target components, processes of separation of rare earth and other metals have been implemented. In addition, this method is easily scalable, that is, it is applicable not only in laboratory conditions, but also on an industrial scale [15,16].

The use of extraction systems based on water-soluble polymers is a more environmentally friendly method. Traditionally, for the extraction of V(IV) [17], Hg(II), Co(II), Zn(II) [18] and Tl(I) [19] ions, it is carried out using toxic and flammable organic solvents, but this can avoid if using aqueous two-phase systems. In addition, they allow efficient extraction of metals such as Fe(III), Ni(II), La(III), Ce(III). These systems are an environmentally friendly replacement for organic solvents. However, with all the obvious advantages of ATPS, there is a number of weaknesses. So, for example, in [20] was shown that wide range of metals is extracted without selectivity, which necessitates their additional separation. Another problem is the initial medium from which metals are extracted. For example, it has been shown to extract such metals as Fe(III), Co(II), Cu(II) [21, 22], Co(II) and Ni(II) [23], Fe(III) [24] in ATPs from sulfate media, which requires additional introduction into the system of complexing agents such as potassium thiocyanate or 1-nitroso-2-naphthol, which entails the problem of waste disposal after extraction. In addition, attention is paid to liquid-liquid equilibria of aqueous two-phase systems, which can subsequently be used for extraction processes [25, 26]. Research also concerns the extraction of Fe(III), Co(II), Cu(II) and Ni(II) from chloride media [27].

It should be noted that in [28] was shown the extraction of metals using a quaternary ammonium base (QAB) (Aliquat 336) in an aqueous two-phase system with high efficiency, which is caused by the formation of metal complexes with Aliquat 336. However, despite the high metals distribution coefficient, QABs are toxic and do not satisfy the requirements of «green» chemistry.

In [29] was studied the extraction of a number of alkali and transition metal chlorides from aqueous media using DESs based on decanoic acid and lidocaine in various ratios (2:1, 3:1, 4:1). The study showed that most metal cations are extracted with high efficiency.

In this regard, the aim of this work was synthesis DES based on polypropylene glycol 425 (PPG425) and tetrabutylammonium bromide (TBAB) and its application for extraction the range of metals: Fe(III), Zn(II), Cu(II), Ni(II), Co(II), Mn(II).

2. Experimental

The tools were used in this work: 50 ml measuring beakers, measuring pipettes (from 10µ to 5ml), 20 ml separation funnels, 15 ml graduated plastic tubes, drop tube, analytical Balance (AND HR-100AZ), Magnetic stirrer with heating plate (IKA C-MAG HS4) with stirrer bar, centrifuge (ELMI CM-6MT), desalinated filter paper, Enviro-Genie thermostatically controlled shaker (Scientific Industries, Inc.), spectrophotometer Cary-60 device (Agilent Tech.), quartz cuvettes (l=10mm)

The initial solutions of metal chlorides or nitrates were prepared by dissolving precise weights of FeCl₃·6H₂O, ZnCl₂, NiCl₂·6H₂O, CoCl₂·6H₂O, MnCl₂·4H₂O, CuCl₂·2H₂O with the qualification of “chemical grade” in distilled water suspended on an analytical balance (AND HR-100AZ).

DES based on PPG-425 and TBAB in (2:1) mole ratio were used as the extractant. The molar ratio was chosen based on literatures data, in which similar DES were successfully synthesized and applied [30,31]. This extractant was prepared at a temperature of 80°C with constant mixing for 10 minutes. By
the method of IR spectroscopy was confirmed the formation of hydrogen bonds between PPG-425 and TBAB, which indicates the DES formation.

The extraction of metal ions was carried out using an aqueous two-phase system based on DES(33 wt.%) - NaCl(8 wt.%) - H2O with an initial metal concentration of 0.01mol L⁻¹ and a hydrochloric acid concentration in the salt phase of 0.03mol L⁻¹, for suppression of the hydrolysis reaction. The ratio of polymer and salt phases was 1:3.

The extraction of metal ions (Fe(III), Zn(II), Cu(II), Ni(II), Co(II), Mn(II)) was carried out at a temperature of 25°C in graduated plastic tubes in a thermostatic Enviro-Genie shaker (Scientific Industries, Inc.) at a rotation speed of 30 rpm to establish thermodynamic equilibrium (20 min).

The concentration of metal ions in the initial solutions and in the aqueous phases after extraction was determined spectrophotometrically using 4-(2-pyridylazo)resorcinol, which forms complexes with metals that absorb in the visible spectrum at the following wavelengths: Zn (490 nm), Ni (492 nm), Co (508 nm), Mn (496 nm), Cu (494 nm). To determine Fe (III), sulfosalicylic acid was used, with a maximum absorption of complex at a wavelength of 420 nm. The concentration of metal ions in the organic phases was determined by the difference between the concentrations in the initial solution and in the aqueous phase after extraction, taking into account the ratio of phase volumes. The optical density values were determined using a Cary-60 device (Agilent Tech.) in quartz cuvettes $l = 10$ mm.

The presented experimental data are unique and are the result of a series of experiments and processed by methods of mathematical statistics.

3. Results and discussion
We studied the interphase distribution of a wide range of metal ions (Fe(III), Zn(II), Cu(II), Ni(II), Co(II), Mn(II)) in the system based on DES(33 wt.%) - NaCl(8 wt.%) - H2O. Figures 1 and figures 2 shows the values of the distribution coefficients and the extraction efficiency for the listed metal ions.

![Fig. 1. The values of the distribution coefficients for the metal ions extracted in an aqueous two-phase system based on DES(PPG-425 - TBAB)-NaCl- H2O](image-url)
Based on the data from figures 1 it is obvious that only Fe(III) and Zn(II) are well extracted, the distribution coefficients (D) are 71.64 and 25.17, respectively, for the rest metals distribution coefficients do not exceed 0.4. It is possible that the high values of the distribution coefficients for iron and zinc are associated with the fact that they easily forming chloride complexes, which is not typical for other metals.

4. Conclusions
The study showed the effectiveness of using DES based on PPG-425 and TBAB in the extraction of a number of metal ions by the system DES(33 wt.%) - NaCl(8 wt.%) - H2O. It was found that using DES it is possible to achieve not only high extraction efficiency of Fe(III) and Zn(II), but also selective extraction of these metals in comparison with a number of studied metals. Thus, it is possible to use DES based on PPG-425 and TBAB (2:1) mole ratio for the selective extraction of Fe(III) and Zn(II) from aqueous media.

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