Extraction of Zn (II) ions in an polypropylene glycol 425 – sodium chloride - water aqueous two-phase system

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Abstract. Liquid-liquid extraction is one of the most used separation methods in chemical technology for recovery and separation of metal ions, other inorganic and organic substances. It is known that for extraction of Zn(II) the most frequently used extractants are D2EHPA, Aliquat 336, etc., diluted in an organic solvent. The use of these reagents does not meet the principles of "green" chemistry. Thus, in the present work, the extraction system based on polypropylene glycol 425 and sodium chloride for the extraction of Zn(II) ions from aqueous solutions is proposed. Equilibrium values of the distribution coefficient in the proposed aqueous two-phase system have been determined. Dependence of metal distribution coefficient on time of phase contact is obtained, time to reach equilibrium was 10 minutes. The isotherm of Zn(II) extraction obtained in the proposed system is a straight line, which indicates the independence of the distribution coefficient from the initial concentration of metal in the solution. The received experimental data can be used at the creation of "green" schemes of processing of Ni-MH batteries.

Keywords: aqueous two-phase system, extraction, polypropylene glycol, sodium chloride, Ni-MH battery

1. Introduction

Nickel-metal hydride (Ni-MH) batteries are widely used as energy sources [1]. However, improper disposal of electronic waste can lead to environmental pollution as well as harm to human health. The products of primary processing of Ni-MH batteries contain a large number of strategically important metals (Ni, Co, Mn, Zn, La, Ce, etc.) [2,3]. The hydrometallurgical method is the most promising way to extract metals from used chemical power sources, due to the advantages of high metal recovery efficiency and high purity of the product. The leaching process allows obtaining a solution containing a large number of metals for subsequent separation and recovery.

Extraction is a popular method used in chemical and technological processes for:
1) recovery of biologically active compounds (proteins, cells, DNA/RNA, vitamins, etc.) from aqueous media [4,5];
2) purification of hydrocarbons from sulfur, nitrogen, and aromatic substances [6,7];
3) recovery of organic acids from fermentation solutions [8-10];
4) extraction and separation of rare-earth [11], precious [12], non-ferrous [13], radioactive elements [14,15] and others.

Recent works present the results of metal extraction using neutral and ion-exchange extractants – TBP, Cyanex 272, D2EHPA, PC 88A, ionic liquids, binary extractants, and others [16, 17]. Gupta et al. studied Cd extraction in the presence of accompanying metals (Ni, Co, Fe, Mn, Al, Hg, etc.) using commercial extractant Cyanex 923 [18]. Belova et al. studied the extraction of rare-earth metals from chloride and nitrate solutions using binary extractants based on Aliquat 336, D2EHPA, Cyanex 272, etc. [19,20]. The effective extraction of lanthanides in such systems is shown.

Aghdam et al. studied the extraction of Zn(II) from chloride media by solvent extraction using D2EHPA. Quantitative extraction of zinc was achieved at double excess of D2EHPA and medium acidity (pH) from 3 to 6 [21]. Spathariotis et al. studied the extraction of Zn(II) from deep eutectic solvent using Aliquat 336. Using Aliquat 336, which was not diluted with solvent, 80 % zinc extraction was achieved [22].

However, the use of toxic and explosive organic solvents negatively affects the environment and humans [20]. Nowadays such direction of extraction chemistry as aqueous two-phase systems based on ecologically safe water-soluble polymers meeting the principles of "green" chemistry is intensively developing [23]. Aqueous two-phase systems also find application for the extraction and purification of biologically active substances [24], organic acids [25-27], metal salts [28].

Extraction and recovery of zinc from hydrometallurgical processing solutions is an urgent task for today, as the emission of such waste is regulated by environmental legislation. Previously, zinc extraction from aqueous solutions using ATPS based on polypropylene glycol was not carried out. In this work, we studied for the first time the interphase distribution of Zn(II) in the eco-safety extraction system of PPG 425 - NaCl - H₂O. The time of metal ion equilibrium achievement between polymeric and salt phases has been determined. The extraction isotherm Zn(II) in the proposed system was obtained. The results of this work show that the system based on polypropylene glycol is no less effective than the classical extraction systems.

2. Experimental

2.1. Reagents and instruments

The tools and materials were used in this work: 50 ml measuring beakers, measuring pipettes (from 100µ to 5ml), 20 ml separation funnels, 15 ml graduated plastic tubes, analytical Balance (AND HR-100AZ), 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 ATPS was made by mixing precise weigh of sodium chloride with the qualification of “chemical grade”, precise volume of polypropylene glycol 425 and precise volume of distilled water.

The initial solutions of metal chlorides or nitrates were prepared by dissolving precise weights of ZnCl₂ with the qualification of “chemical grade” in distilled water suspended on an analytical balance (AND HR-100AZ).

2.2. Research methods.

The extraction of metal ions was carried out using an aqueous two-phase system based on polypropylene glycol 425 (30 wt.%) – NaCl (8 wt.%) - H₂O with an initial metal concentration of 0.01mol L⁻¹. The ratio of polymer and salt phases was 1:3. To prevent the formation of insoluble zinc hydroxide in the system was introduced hydrochloric acid in the amount of 0.00012 mol. The extraction of metal ion (Zn (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 (30 min).
The evaluation of extraction efficiency was carried out using characteristics such as distribution coefficient (D) calculated using formulas (1):

\[ D = \frac{C_{t,ph}}{C_{b,ph}}, \]  

(1)

where \( C_{t,ph} \) – metal concentration in top (polymer) phase, \( C_{b,ph} \) – metal concentration in bottom (salt) phase.

The concentration of Zn ion in the initial solutions and the top and bottom phases after extraction was determined spectrophotometrically using 4-(2-pyridylazo)resorcinol, which forms complexes with metals that absorb in the visible spectrum at the wavelength of 492 nm. The optical density values were determined using a Cary-60 device (Agilent Tech.) In quartz cuvettes \( l = 10 \text{ mm} \).

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

3. Results and discussion

We have carried out a study on the interphase distribution of Zn(II) ions in the polypropylene glycol 425 (30 wt %) - NaCl (8 wt %) - H\(_2\)O system. We studied the effect of phase contact time on zinc ion extraction. Figure 1 shows the kinetic dependence of the Zn(II) ions distribution coefficient. As can be seen from Fig. 1, phase contact time practically does not affect the interphase distribution of ZnCl\(_2\). In this case, the equilibrium is achieved already at mixing time equal to 10 minutes.

![Figure 1. Dependence of Zn(II) ion distribution coefficient on phase contact time in PPG 425 (30 wt. %) - NaCl (8 wt. %) - H\(_2\)O system, C(Zn(II))\(_{\text{init}}\) = 0.01 mol L\(^{-1}\).](image)

Further, we studied the influence of initial metal concentration on the distribution coefficient. For this purpose, we carried out an experiment on the variation of the initial concentration of ZnCl\(_2\) from 0.001 to 0.01 mol L\(^{-1}\) in PPG 425 (30 wt. %) - NaCl (8 wt. %) - H\(_2\)O system. Figure 2 shows the extraction isotherm. As can be seen from Figure 2, the extraction isotherm has a straightforward character, which suggests that the initial concentration of metal (in the range under study) does not affect the distribution coefficient.
Figure 2. Isotherm of extraction of Zn(II) ions in PPG 425 (30 wt. %) - NaCl (8 wt. %) - H$_2$O system.

It should be noted that similar results on metal extraction in this system were obtained earlier for Fe(III) Zakhodyaeva and others [28]. In the work of Zakhodyaeva et al. [29], the distribution of zinc and other non-ferrous metals ions in the system with polyethylene glycol 1500 was studied. In the PEG 1500 (16.3 wt.% - NaNO$_3$ (36 wt.% - H$_2$O system phase contact time and initial metal concentration also do not influence the zinc distribution coefficient. In the works of Fedorova et al. the extraction of Zn(II) ions is described in PPG 425 (30 wt. %) - NaCl (8 wt. %) - H$_2$O system with the introduction of complex-forming agents of organic nature [30-31]. In these works, the mechanism by which zinc is extracted from hydrochloric acid solutions was proposed. Extraction occurs due to the formation of chloride anion complexes, composition [ZnCl$_4$]$^{2-}$.

4. Conclusion
In the course of the research, we obtained quantitative characteristics of Zn(II) ion extraction in PPG 425 (30 wt. %) - NaCl (8 wt. %) - H$_2$O system. It was found that the contact time of phases, as well as the initial concentration of Zn(II) ions, do not affect the degree of metal extraction. It was shown that this system is promising for extracting this metal from acidic aqueous solutions. The data obtained can be used to solve the problems of zinc extraction from hydrochloric acid solutions.

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Acknowledgments
The reported study was funded by RFBR and Moscow city Government according to the research project № 19-33-70011.