The interphase distribution of light REE Ce(III) and La(III) in system based on PEG-1500 – NaNO₃ – H₂O with the quaternary ammonium base addition

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Abstract. The problem of e-waste processing and recovery of valuable metals from such waste for the second use is attracting more and more scientists’ attention. Liquid extraction as one of hydrometallurgy steps is a traditional method for the metal recovery. However, application of solvent extraction is not meet the green chemistry principles due to organic solvents. Aqueous two-phase systems based on water-soluble polymers are promising alternative for hazardous organic solvents. In this work the dependencies of Ce(III) and La(III) distribution coefficients from process time and the initial quaternary ammonium base concentration have been achieved. Also, based on the Ce(III) and La(III) extraction isotherms it has been shown that the metals initial concentrations are highly affects the distribution coefficients of studied metals. The possibility of aqueous two-phase system application as a solvent for quaternary ammonium salt for light REE (Ce(III) and La(III)) extraction from water solution has been shown.

Key words: liquid extraction, aqueous two-phase systems, rare earths elements extraction, waste processing, «green» chemistry

1. Introduction
The increase in demand, and, as a consequence, the consumption of electronic devices around the world is constantly growing [1-3]. In that case, the amount of e-waste containing valuable components, including rare-earth metals (Ce, La, etc.) is increasing [4,5]. The problem of processing such kind of waste and extracting valuable metals from them, for their reuse, is a key one, since the storage of chemical current sources entails environmental pollution by heavy metals [6]. To implement this task, one of the promising stages of the hydrometallurgical process - liquid extraction can be use [7-10]. For example, the possibility of rare earth elements [11-13], some actinides [14] and iron ions [15,16] extraction with binary organic extragents has been shown. However, the application of traditional approaches is connected with organic solvents that make extraction processes expensive and environmental unsafe [17]. Also, using strong acids in extraction and re-extraction processes is required complicated waste utilization processes after the recovery of valuable components [18].

The promising alternative for the hazardous organic solvents can be aqueous two-phase systems based on water-soluble polymers that are biodegradable, fire-resistant and safe [19-21]. Moreover, such systems can extract the range of metals from aqueous media with high effectivity and selectivity [22-25].
The aim of this work was the investigation of quaternary ammonium base salt effect on the light rare-earth elements (Ce(III) and La(III)) extraction in aqueous two-phase system based on polyethylene glycol 1500. The influence of the phase contact time on the distribution coefficients of Ce(III) and La(III) has been determined. Also, effects of the initial concentration of metals and quaternary ammonium base salt on the Ce(III) and La(III) distribution coefficients in aqueous two-phase system has been investigate.

2. Experimental details

2.1. Reagents

The initial solutions of metal nitrates were obtained by dissolving the sample weights of La(NO$_3$)$_3$•6H$_2$O and Ce(NO$_3$)$_3$•6H$_2$O of the qualification “chemical grade” suspended on an analytical balance (AND HR-100AZ) in distilled water. Trioctylmethylammonium nitrate (TOMAN) was prepared as follows: 1.6 mol L$^{-1}$ sodium nitrate solution was mixed with Aliquat 336 in a 1:1 ratio [26]. Stirring was performed until the chloride ions were completely replaced by nitrate ions. The mixing time was 20 minutes.

2.1.1. Research methods

The metal ions extraction was carried out using a two-phase aqueous system polyethylene glycol 1500 (16.3%) - NaNO$_3$ (36%) - H$_2$O with an initial metal concentration of 0.01 mol L$^{-1}$ (except for the cases when the investigations on the effects of the initial concentrations of metals on the distribution coefficients were carried out). The nitric acid concentration in the salt phase was equal 0.01 mol L$^{-1}$ (for the hydrolyze avoiding).

The metal ions La (III) and Ce (III) extraction was carried out at a temperature of 25°C in graduated plastic tubes in an Enviro-Genie thermostatically controlled shaker (Scientific Industries, Inc.) at a rotation speed of 30 rpm until the thermodynamic equilibrium was established (20 min).

The complexometric titration using EDTA and xylenol orange at pH = 6 was used to determine the metal ions concentration in the initial solutions and in the aqueous phases after extraction.

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

3. Results and discussion

To 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. The dependence Ce(III) and La(III) distribution coefficients on the phase contact time in system based on PEG-1500 (16.3%) – NaNO$_3$ (36%) – H$_2$O, [Me]$_{init.}=0.01$ mol L$^{-1}$, [TOMAN]$_{t.p.}=0.05$ mol L$^{-1}$.](image-url)
To determine the effect of the metals initial concentration on the Ce(III) and La(III) distribution coefficients, the extraction isotherms of both metals were obtained Figure 2. Based on the Figure 2, it is clear that the extraction isotherms of both metals have a similar form - they increase over the entire studied interval from [Me]0.001 to 0.01 mol L⁻¹.

![Figure 2](image_url)

**Figure 2.** Ce(III) and La(III) extraction isotherms in system based on PEG-1500 (16.3%) – NaNO₃ (36%) – H₂O, [TOMAN]ₜ.p.=0.05 mol L⁻¹, where [Me]ₜ.p. mol L⁻¹ – metal concentration in the equivalent top phase, [Me]ₜ.p. mol L⁻¹ – metal concentration in the equivalent bottom phase.

The Figure 3 shows the dependence of the Ce(III) and La(III) distribution coefficients on the TOMAN initial concentration in the top phase. It can be clearly seen the exponential nature of the graph – from the [TOMAN]=0.07 mol L⁻¹ there is a sharp increase in the Ce(III) and La(III) distribution coefficients.

![Figure 3](image_url)

**Figure 3.** The dependences of Ce(III) and La(III) distribution coefficients on the TOMAN initial concentration.
4. Conclusions

As a result of this work Ce(III) and La(III) extraction isotherms at temperature of 25°C in the system based on PEG-1500 – NaNO₃ – H₂O with the TOMAN addition has been obtained. The nonlinear nature of these dependences indicates that the distribution coefficients of Ce(III) and La(III) strongly depend on the initial metals concentrations. Obtained kinetic dependences of Ce(III) and La(III) distribution coefficients shows that in case of Ce(III) the dependence slightly increases through the studied period, and in case of La(III) this dependence has a maximum (at 20min) and then decreasing (possibly because of emulsification process). The obtained dependences of the distribution coefficients of Ce (III) and La (III), depending on the initial concentration of TOMAN, show that with a seven-fold excess of TOMAN in the upper phase, the distribution coefficient of La (III) equals 100. This work shows the possibility applying aqueous two-phase systems as an alternative solvent for traditional organic solvent.

References

1. Zhang L, Lijuan L, Rui H, Shi D, Peng X, Ji L, Song X 2020 Lithium recovery from effluent of spent lithium battery recycling process using solvent extraction J. Hazard. Mater. 398 122840
2. Nowakowski P, Pamula T 2020 Application of deep learning object classifier to improve e-waste collection planning Waste Manag. 109 1-9
3. Ismail H, Hanafiah M M 2020A review of sustainable e-waste generation and management: Present and future perspectives J. Environ. Manage. 264 110495
4. Kumari A, Panda R, Lee J, Thriveni T, Jha M, Pathak D 2019 Extraction of rare earth metals (REMs) from chloride medium by organometallic complexation using D2EHPA Sep. Purif. Technol. 227 115680
5. Zhang J, Li X, Song D, Miao Y, Song J, Zhang L 2018 Effective regeneration of anode material recycled from scrapped Li-ion batteries J. Power Sources 390 38-44
6. Li W, Achal V 2020 Environmental and health impacts due to e-waste disposal in China–A review Sci. Total Environ. 737 139745
7. Granata G, Pagnanelli F, Moscardini E, Takacova Z, Havlik T, Toro L 2012 Simultaneous, Recycling of nickel metal hydride, lithium ion and primary lithium batteries: Accomplishment of European Guidelines by optimizing mechanical pre-treatment and solvent extraction operations J. Power Sources 212 205-11.
8. Fedorova M I, Zinov’eva I V, Zakhodyaeva Y A, Voshkin A A 2020 Extraction of Fe(III), Zn(III), and Mn(II) using a system with a Green Solvent for trioctylmethylammonium thiocyanate Theor. Found. Chem. Eng. 54 2 313-8
9. Takahashi V C I, Botelho Junior A B, Espinosa D C R, Tenorio J A S 2020 Enhancing cobalt recovery from Li-ion batteries using grinding treatment prior to the leaching and solvent extraction process J. Environ. Chem. Eng. 8 103801
10. Shuya L, Yang C, Xuefeng C, Wei S, Yaqing W, Yue Y 2020 Separation of lithium and transition metals from leachate of spent lithium-ion batteries by solvent extraction method with Versatic 10 Sep. Purif. Technol. 250 117258
11. Belova V V, Voshkin A A, Egorova N S, Kholkin A I 2012 Solvent extraction of rare earth metals from nitrate solutions with di(2,4,4-trimethylpentyl)phosphinate of methyltriocylammonium J.Mol. Liq. 172 144-6
12. Belova V V, Voshkin A A, Egorova N S, Khol’kin A I 2010 Extraction of rare earth metals from nitrate solutions with a binary extractant based on Cyanex 272 Rus. J. Inorg. Chem. 55 4 629-33
13. Belova V V, Voshkin A A, Egorova N S, Khol’kin A I 2015 Extraction of rare earth metals, uranium, and thorium from nitrate solutions by binary extractants Theor. Found. Chem. Eng. 49 4 545-9
14. Egorova N S, Belova V V, Voshkin A A, (…) Pyartman A K, Keskinov V A 2008 Extraction of uranyl nitrate with a binary extractant based on di(2,4,4-trimethylpentyl)phosphinic acid *Theor. Found. Chem. Eng.* **42** 5 708-13

15. Voshkin A A, Belova V V, Khol’kin A I 2003 Extraction of iron(II) by binary extractants based on quaternary ammonium bases and organic acid *Rus. J. Inorg. Chem.* **48** 4 608-13

16. Voshkin A A, Belova V V, Zakhodyaeva Y A 2018 Iron extraction with Di(2-ethylhexyl)dithiophosphoric acid and a binary extractant based on it *Rus. J. Inorg. Chem.* **63** 3 387-90

17. Sun Y, Zhu M, Yao Y, Wang H, Tong B, Zhao Z 2020 A novel approach for the selective extraction of Li⁺ from the leaching solution of spent lithium-ion batteries using benzo-15-crown-5 ether as extractant *Sep. Purif. Technol* **237** 116325

18. Batchu N, Sonu C, Lee M 2013 Synergistic solvent extraction of manganese(II) with a mixture of Cyanex 272 and Cyanex 301 from chloride solutions *Hydrometallurgy* **140** 89

19. Zakhodyaeva Y A, Rudakov D G, Solov’ev V O, Voshkin A A, Timoshenko A V 2019 Liquid-liquid equilibrium in an extraction system based on polyvinylpyrrolidone-3500 and sodium nitrate *Theor. Found. Chem. Eng.* **53** 2 159-65

20. Zakhodyaeva Y A, Rudakov D G, Solov’ev V O, Voshkin A A, Timoshenko A V 2019 Liquid-liquid extraction equilibrium of aqueous two-phase system composed of poly(ethylene oxide)1500 and sodium nitrate *J. Chem. Eng. Data* **63** 3 1250-5

21. Oan Y, Sun X, Qi M, Qin R, Che X, Zhang Y 2020 A clean and efficient method for separation of vanadium and molybdenum by aqueous two-phase systems *J. Mol. Liq.* **313** 113540

22. Zakhodyaeva Y A, Zinov’eva I V, Tokar E S, Voshkin A A 2019 Complex Extraction of Metals in an Aqueous Two-Phase System Based on Poly(Ethylene Oxide) 1500 and Sodium Nitrate *Molecules* **22** 22 4078

23. Zakhodyaeva Y A, Izuymova K V, Solov’eva M S, Voshkin A A 2017 Extraction separation of the components of leach liquors of batteries *Theor. Found. Chem. Eng.* **51** 11 883-7

24. Voshkin A A, Zakhodyaeva Y A, Zinov’eva I V, Shkinev V M 2018 Interphase distribution of aromatic acids in the polyethylene glycol – sodium sulfate – water system *Theor. Found. Chem. Eng.* **52** 5 890-3

25. Zakhodyaeva Y A, Zinov’eva I V, Voshkin A A 2019 Extraction of Iron(III) Chloride Complexes Using the Polypropylene Glycol 425–NaCl–H2O *Theor. Found. Chem. Eng.* **53** 5 735-40

26. Nayl A 2010 Extraction and separation of Co(II) and Ni(II) from acidic sulfate solutions using Aliquat 336 *J. Hazard. Mater.* **173** 223

**Acknowledgement**
The reported study was funded by RFBR according to the research project № 18-29-24170