Application of ionic liquid based on Aliquat 336 and D2EHPA in the extraction of transition metals

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Abstract. To date, there are a number of methods for selective extraction of transition metal ions based on liquid-liquid extraction. One of the most interesting methods of metal ions extraction is liquid-liquid extraction with application of ionic liquids based on quaternary ammonium bases and organic acid residues, in particular, organophosphorus, diluted with organic solvent (toluene, xylene, kerosene, etc.). However, using of organic solvents does not correspond to the modern tendencies of harmful effects on the environment reducing. Thus, we propose to use Aliquat 336 and D2EHPA-based ionic liquid for extraction of transition metal ions in ecologically safe aqueous two-phase system based on polypropylene glycol 425 and sodium chloride. Di(2-ethylhexyl)phosphate trioctylmethylammonium has been shown to yield more than 80% Fe(III) and Y(III) ions.

Key words: liquid-liquid extraction, aqueous two-phase systems, ionic liquid, “green” chemistry

1. Introduction

Ionic liquids (IL) based on quaternary ammonium bases and organic acid residues are widely used in the extraction of organic [1] and inorganic substances [2]. Zakhodyaeva et al. [3-5] were studied the distribution of monocarboxylic acids from aqueous phases to organic phase (toluene) with using of ionic liquids that include a quaternary ammonium base (QAB) (trioctylmethylammonium) and an organophosphorus residue (di(2-ethylhexyl)phosphate, di(2-ethylhexyl)dithiophosphate or dinonylnaphthalene sulfonate). In this case, the extraction of organic acids occurs due to the non-covalent interaction between the proton formed by the organophosphorus acid and the anion of the acid residue of the extracted monobasic acid [1]: $H_{\text{aq}}X^+ + R_4N\text{A}_{\text{org}} \leftrightarrow R_4N{\text{X} \cdot HA}_{\text{org}}$. It should be noted that the extraction of monocarboxylic acids by these ionic liquids is characterized by high distribution coefficients, for example, for caproic acid it is 68, for butanoic acid - 34 [2]. Li et al. [6] were studied cresol distribution with using IL based on imidazolium cation and rhodanid anion. It was shown that the extraction efficiency could reach 98% under optimal conditions: temperature 298.15 K, mass ratio IL: model solution = 0.2 and phase contact time – 30 minutes. Sulaiman et al. [7] were studied the range of chlorophenols distribution in system based on water – IL (based on bis(trifluoromethylsulfonyl)imide). The synthesized ILs proved to be effective for the whole range of chlorophenols - the extraction rate was more than 80% in one extraction stage. Skoronski et al. [8] studied the effect of ILs based on
phosphonium cation and organophosphoric acid residue on phenol extraction. At volume ratio of phases water - IL, which is 135, practically quantitative extraction of both 2,4-dichlorophenol and phenol is achieved.

The use of ILs for extraction has found extensive applying in the extraction of inorganic substances: acids [2], rare earth metals [10-12], nonferrous [13,14] and alkali [15] metals. Belovoi et al. [16-19] were studied the distribution of rare-earth metals (REM) using ionic liquids based on phosphoric or phosphoric acids and a methyltrioctylammonium cation. REMs are able to form complex anions (like other metals of side groups) due to coordination interaction with residues of organic and inorganic acids. Pavón et al. [20] had described the REM extraction mechanism with using IL based on organic base and phosphoric acid. It can be presented by following way:

\[
3RNH_3^+A_{(org)}^- + Me_{3(aq)}^+ + 3Cl_{(aq)}^- \leftrightarrow MeA_3 \cdot 3RNH_3^+Cl_{(org)}^-.
\]

Voshkin et al. [21-22] had described iron (III) extraction mechanism with using IL based on quaternary ammonium base and organic acid. In general, it can be presented by following equation:

\[
12FeCl_4_{(aq)}^- + 9R_4NA_{(org)} \leftrightarrow 9(R_4N)FeCl_4_{(org)} + Fe_3A_9_{(org)} + 12Cl_{(aq)}^-.
\]

One of metal ionic liquids advantages is easier re-extraction than in case of using only organophosphoric acids, due to the complex compound with ammonium base formation. Thus, the use of ionic liquids makes it possible to combine cation-exchange and anion-exchange extraction.

However, organic solvents application does not meet the principles of "green chemistry": they are toxic and flammable. Therefore, it is necessary to find an environmentally friendly replacement for them. One of the most developing directions is the creation of two-phase water systems based on water-soluble polymers [23] and their use for the extraction of metal ions both without the introduction of complexing agents [24] and with the introduction of such agents [25-27], these systems may be an alternative to organic solvents.

Thus, the goal of this work was to study the effect of an ionic liquid based on a quaternary ammonium base and organophosphorus acid on the extraction of a number of transition metals in an aqueous two-phase system.

2. Experimental details

2.1. Reagents

The tools and materials were used in this work: 50 ml measuring beakers, measuring pipettes (from 100µl to 5ml), 20 ml separation funnels, 15 ml graduated plastic tubes, drop tube, analytical Balance (AND HR-100AZ), Magnetic stirrer (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, NiCl₂ · 6H₂O, CoCl₂ · 6H₂O, MnCl₂ · 4H₂O, and Y(NO₃)₃ · 6H₂O with the qualification of “chemical grade” in distilled water suspended on an analytical balance (AND HR-100AZ).

An ionic liquid based on trioctylmethylammonium chloride (Aliquat 336) and di(2-ethylhexyl)phosphoric acid (D2EHPA) was used as an extractant. This extractant was made by mixing of equal amounts of Aliquat 336 and D2EHPA during 20 minutes followed by stripping with alkali of organic phase for chloride-ions removing.

2.1.1. 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.

The extraction of metal ions (Fe (III), Ni (II), Co (II), Mn (II), Y(III)) 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) and extraction degree (E, %) calculated using formulas (1) and (2):

\[ D = \frac{C_{t, ph.}}{C_{b, ph.}}, \quad (1) \]

\[ E = \frac{C_{t, ph.} \cdot V_{t, ph.}}{C_{t, ph.} \cdot V_{t, ph.} + C_{b, ph.} \cdot V_{b, ph.}}, \quad (2) \]

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

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: Ni (492 nm), Co (508 nm), Mn (496 nm). To determine Fe (III), sulfosalicylic acid was used, with a maximum absorption of complex at a wavelength of 420 nm. The complexometric titration using EDTA and xylene orange at pH = 6 was used to determine the Y(III) ions concentration in the initial solutions and in the aqueous phases after extraction. 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
The investigation on a wide range of metals (Fe(III), Ni(II), Co(II), Mn(II), Y(III)) interphase distribution in system based on polypropylene glycol 425 (30 wt.%), NaCl (8 wt.%), H2O with trioctylmethylammonium di(2-ethylhexyl)phosphate ionic liquid has been carried out. It should be noted, that there is a possibility of precipitate formation (tri-phase system consisted of two liquids and one solid phases) for individual metals (Fe(III), Y(III)) that can be dissolve by hydrochloric acid or extra amounts of ionic liquid (IL) addition. Thus, for the Fe(III), Y(III) ions the conditions under which the formed system is two-phase (consisting of two liquid phases) have been determined.

Quantitative characteristics of metal ions extraction are shown in Table 1. This table contains also data about conditions (hydrochloric acid and trioctylmethylammonium di(2-ethylhexyl)phosphate concentrations) required for heterogeneous system formation.

| Table 1. The quantitative characteristics of metal ions extraction in ATPS with ionic liquid addition |
| --- |
| | C(IL), mol L\(^{-1}\) | C(HCl), mol L\(^{-1}\) | \( C_{b,p,h.} \), mol L\(^{-1}\) | \( C_{t,p,h.} \), mol L\(^{-1}\) |
| Fe(III) | 0.1 | 1.25 | 0.00037 | 0.023 |
| Ni(II) | 0.1 | 0 | 0.012 | 0.00 |
| Co(II) | 0.1 | 0 | 0.010 | 0.00 |
| Mn(II) | 0.1 | 0 | 0.07 | 0.00076 |
| Y(III) | 0.4 | 1.07 | 0.0003 | 0.019 |

It can be seen from figure 1 and figure 2 that obtained extractant is effective for following metals: Fe(III) and Y(III) as they are capable for complex compounds formation with the D2EHPA residue and QAB cation, which were shown in works by Voshkin [21-22], Fedorova [26], Tait [27], Mishra [28]. At the same time for Ni(II), Co(II) and Mn(II) ions this extractant was not effective, which was also shown in Tait [27]. This may be due to the fact that these metals are unable to form complex compounds with organophosphoric acid residual and QAB cation in similar media. Also di(2-ethylhexyl)phosphate trioctylmethylammonium extract Y(III) ions. This may be due to the fact that the radius of yttrium ion...
is small and inclined to complex formation [28]. Thus, with using this extragent it is possible almost quantitative extraction of these metals, and metal ions effective separation.

![Figure 1. The distribution coefficients of metals in ATPS with IL addition](image1.png)

![Figure 2. The extraction efficiency of metals in ATPS with IL addition](image2.png)

4. Conclusions

In the course of the study, quantitative characteristics of the extraction of transition metal ions in an aqueous two-phase system based on a water-soluble polymer with the introduction of trioctylmethylammonium di(2-ethylhexyl)phosphate were obtained. It was found that this extractant selectively extracts ions of metals such as Fe(III) and Y(III). Thus, it is possible to use trioctylmethylammonium di(2-ethylhexyl)phosphate at certain stages of the implementation of technological schemes, for example, in the separation of metals from leaching solutions using an environmentally friendly extraction system.

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