CHEMISTRY AND TECHNOLOGY OF RARE, TRACE, AND RADIOACTIVE ELEMENTS

Scandium Extraction from Chloride Solutions by a Mixture of Tributyl Phosphate and Molecular Iodine

V. I. Kuz'min[a], * and A. A. Kuz'mina[b]

[a]*Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia*
[b]*Siberian Federal University, Krasnoyarsk, 660041 Russia*
*e-mail: kuzmin@icct.ru

Abstract—It has been established that the addition of elemental iodine significantly enhances the extraction of scandium by means of tributylphosphate. The metal distribution coefficients exhibit an increase with increasing TBP and iodine concentration in the organic phase as well as with increasing chloride ion concentration in the aqueous phase. As an outsalting agent, chlorides of alkali, alkaline earth and other weakly extracted metal cations can be used. The process is promising for the extraction of scandium from solutions of hydrochloric-acid leaching of mineral and man-made materials.

INTRODUCTION

Interest in scandium in recent years has significantly increased, the fields of its application have been broadened. In particular, aluminum alloys with scandium additives can be welded, so are considered very promising for widespread use in aerospace engineering. It is expected that soon the scale of scandium consumption will significantly increase. Some hold that the world is on the threshold of the third "scandium boom" [1].

Scandium belongs to the trace metals; it is rarely found in the form of its own rich ores. It represents a companion of rare earth metals, uranium, thorium and some others.

In view of its low content, the extraction of scandium and its purification is not an easy task, especially if it concerns the processing of man-made materials. One of the important technological problems consists in the development of processes for a selective extraction of scandium from hydrochloric-acid leaching solutions with a complicated composition.

To solve this problem, one can use different classes of extractants. As far as cation-exchange extractants are concerned, a process of scandium isolation via the extraction by di(2-ethylhexyl) phosphoric acid (D2EHPA) is well known [2], including the use of this reagent in the composition of so-called solid extractants [3]. However, along with scandium, a large number of other elements can be extracted in the organic phase. In addition, the reextraction of the metal is hampered to a considerable extent, which requires the use of expensive hydrofluoric acid or water-soluble fluorides. To suppress the extraction of impurities and to facilitate the reextraction of scandium, the authors of [4] investigated the extraction of scandium and some metal impurities by the salts of D2EHPA and ammonium bases.

For neutral extractants, as a rule, the reextraction of metals is not a big problem. The method for scandium extraction by tributylphosphate is well known [5–7]. The disadvantage of this process consists in low scandium distribution coefficients and, as a consequence, the need to use very high concentrations of outsalting agents to increase the extraction level, as well as large volumes of the organic phase in relation to water.

A number of literature sources noted that the addition to chloride solutions of salts with large and weakly hydrated anions in the TBP systems leads to a significant increase in scandium distribution coefficients. The authors of [8] reported a significant increase in the extraction of scandium from mixed chloride–sodium and chloride–perchlorate solutions in comparison with the solutions of individual salts. The authors suggested that this can be caused by the extraction of mixed-ligand scandium salts into the organic phase.

The extraction of scandium with TBP is enhanced to a considerable extent in the presence of iron (3+) anionic complexes such as $FeCl_4^-$ [9]. A disadvantage of the technological process consists in the problem of $HFeCl_4$ preservation in the extraction system. This

complex acid is destroyed in neutral (weakly acidic) media is redistributed between the aqueous and organic phases, which significantly complicates the process and makes it impossible to reextract scandium with water without an almost complete removal of iron chlorides together with the reextract.

Apparently, for the same reason, the extraction of mixed-ligand chloride complexes is associated with an enhancement of the extraction of scandium from bromide–indium solutions by tributyl phosphate, which was discovered by A.B. Sokolov and Yu.A. Zolotov [10]. The increase in the distribution coefficients when adding indium to bromide solutions was observed only for scandium, whereas for the other metal impurities the increase in indium concentration led to a suppression of their extraction level.

The authors of [11] have confirmed the assumption of an increased stability of mixed-ligand scandium complexes in the systems with TBP such as $ScCl_xB_{(3-x)} \cdot L_p$ (here, B is a weakly hydrated anion, L is a molecule of TBP) revealing a significant increase in the extraction of scandium chloride in the mixtures of TBP with molecular iodine. In these systems, molecular iodine can form fairly large, slightly hydrated complex anions together with halide anions such as ClI_2^- and $Cl(I_2)_2^-$,

This work was aimed at an evaluation of the prospects for using this system to develop new technologies for the extraction and purification of scandium from chloride solutions of complicated composition.

EXPERIMENTAL

In the experiments, chemically pure and analytical grade tributylphosphate, toluene, iodine, mineral acids and their salts were used.

The initial organic phase was prepared via dissolving the samples of molecular iodine in a solution of tributyl phosphate in toluene. It was first established that iodine solutions in TBP are sufficiently stable and for a few days there was no significant decrease in iodine concentration in the organic phase. Nevertheless, in order to prevent possible photochemical reactions, the prepared extractant was stored in the dark.

The extraction was carried out via mechanical stirring of the organic and aqueous phases in separating funnels at a temperature of 25°C. The time equilibrium was established was determined from the dependence of the distribution coefficients of the extracted substance on the duration of mixing. It was shown that duration of phase contact ranging from 3 to 5 min is sufficient to achieve constant values of the distribution coefficients. The extraction was carried out mainly at an equal ratio between the volumes of the phases.

After the process was complete, the phases were separated, the analyzed solutions were then filtered to prevent an admixture of the second phase. To determine the concentration of salts in the organic phase, they were previously reextracted with water after a fivefold dilution of an aliquot of the extract five times with toluene, followed by analysis of the aqueous solutions. The concentration of scandium in solutions was determined mainly by means of a spectrophotometric method using alizarin C [12]. In the presence of other metals, the composition of the solutions was determined using an atomic absorption technique (a *PerkinElmer Analist* 400 spectrometer) or mass spectrometric method (an *Agilent 7500A ICP-MS*) method. The content of Cl$^-$ was determined by means of an argentometric titration of aqueous solutions with potassium chromate as an indicator.

RESULTS AND DISCUSSION

It is well known that molecular iodine forms stable complexes with with halide ions such as $Cl(I_2)^-$, $Br(I_2)^-$, I_3^-, and others. Such anions are more hydrophobic than the initial halide ions, which can be used to increase the selectivity of the extraction of halide ions during anion-exchange extraction or the extraction of halide salts in systems with neutral extractants. The authors of one of the first papers in this field [13] showed the possibility of extracting cesium iodides in the form of polyiodide complexes using organic solvents. The authors of [14, 15] proposed a process for extracting calcium bromide from natural calcium chloride solutions using tributyl phosphate and iodine mixtures. During the study of the process, it was established that the recovery is accompanied by the formation of compounds having different compositions, such as $Ca(BrI_2)_2 \cdot pL$, $Ca(ClI_2)(BrI_2) \cdot pL$, $Ca(ClI_2)_2 \cdot pL$ in the organic phase.

The reextraction of recovered salts can be readily carried out using water. In this case, iodine remains in the organic phase, and its loss due to passing to the aqueous solution do not exceed 0.05%.

Figure 1 shows data concerning the extraction of scandium from the solutions of potassium chloride added as an outsalting agent, with tributyl phosphate and different amounts of molecular iodine. As may be seen from the results, iodine additives cause a significant increase in the extraction of scandium from chloride solutions, and when the content of iodine in the organic phase exceeds 0.15 mol/L, the metal distribution coefficient (D_{Sc}) reaches a value of one or greater. It is obvious that this increase is connected with the organic-phase formation of iodine complexes with the chloride ion belonging to the extracted scandium chloride according to the following the interfacial reaction:

$$Sc_{(aq)}^{3+} + 3Cl_{(aq)}^- + pL_{(org)} + I_{2(org)}$$
$$\leftrightarrow ScCl_x(ClI_2)_{(3-x)} \cdot L_{p(org)}. \tag{1}$$
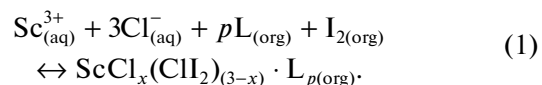
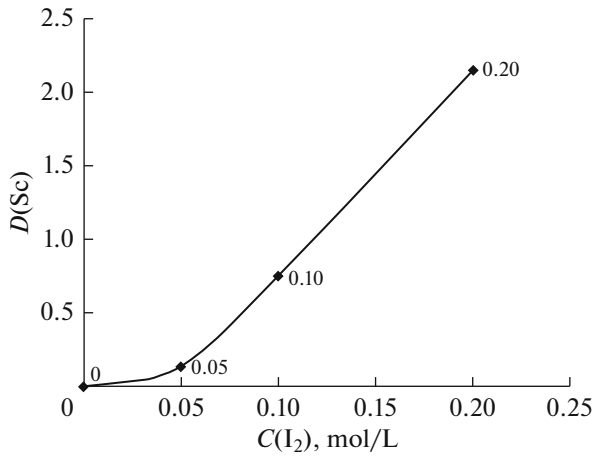Process (1) is written in a simplified form without taking into account the formation of iodine solvates

Fig. 1. Effect of molecular iodine additives on scandium extraction from KCl solutions with tributyl phosphate: organic phase—$C_{TBP} = 80\%$ (in toluene); C_{I_2} = var; water phase—$C_{KCl(ini)} = 5$ mol/L; $C_{ScCl_3(ini)} = 0.05$ mol/L.

with TBP such as $L \cdot I_2$ obviously taking place in these systems. Hereinafter, indices (aq) and (org) denote whether a component belongs to the aqueous or the organic phase, respectively.

The equilibrium constant for this process can be expressed by relationship (2), whereas the value of the distribution coefficient, by relationship (3):

$$K_{(1)} = C_{Sc^{3+}(org)} \Big/ \left(C_{Sc^{3+}(aq)} C^3_{Cl^-(aq)} C^p_{L(org)} C_{I_2(org)} \right) \gamma^4_{\pm}$$
$$= D_{Sc^{3+}} \Big/ \left(C^3_{Cl^-(aq)} C^p_{L(org)} C_{I_2(org)} \gamma^4_{\pm} \right); \quad (2)$$

$$D_{Sc^{3+}} = K_{(1)} C^3_{Cl^-(aq)} C^p_{L(org)} C_{I_2(org)} \gamma^4_{\pm}, \quad (3)$$

where $D_{Sc^{3+}}$ is the scandium distribution coefficient; and $\gamma_{\pm}$ is the average ionic activity coefficient of scandium chloride in a mixed solution.

In accordance with expression (3), an increase in the activity of chloride ions in the aqueous phase owing to the addition of weakly extractable salts (potassium, ammonium, magnesium, etc.) should lead to an increase in the extraction of scandium into the organic phase. Indeed, this takes place, as shown in Fig. 2a. In this case, magnesium chloride was used as an outsalting agent. It can be seen from the data presented that the scandium distribution coefficients in the case of TBP and molecular iodine mixture depending on the concentration of magnesium chloride has a power-law character. In Fig. 2b, the same data are presented in logarithmic coordinates.

The relationship approaches a linear one, however, its slope ratio is about 3.7, instead of the value of 3 which follows from Eq. (3). This discrepancy between the calculated and experimental data is caused, first of all, by changes in the activity coefficients of salts, including scandium chloride, with a significant
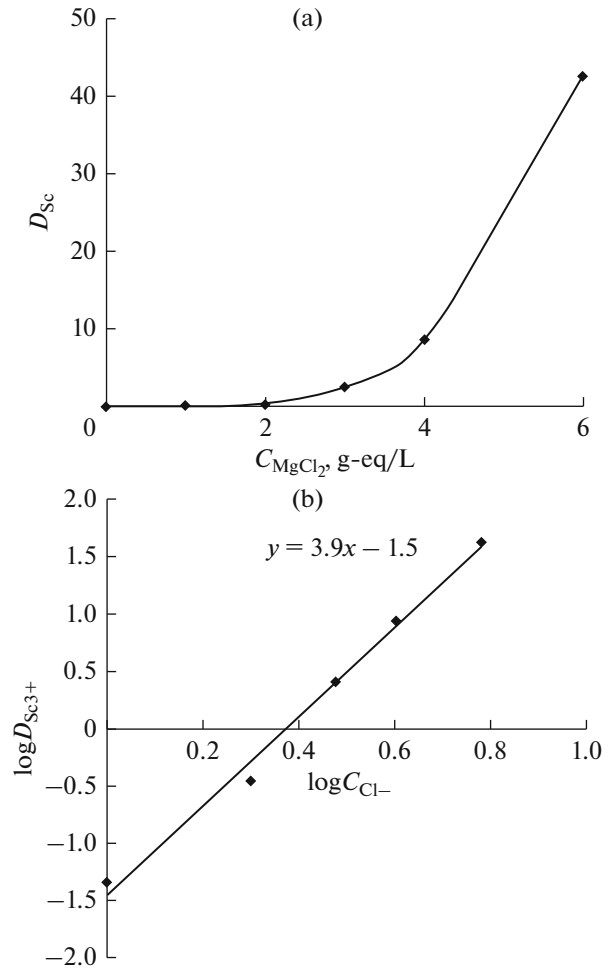

Fig. 2. Effect of outsalting agent (magnesium chloride) concentration on the extraction of scandium chloride by means of aTBP (80%) solution with iodine (0.2 mol/L) in toluene: (a) scandium distribution coefficients depending on magnesium chloride concentration ($C_{MgCl_2(aq)}$, g-eq/L); (b) $\log D_{Sc}$ depending on $\log C_{MgCl_2}$.

change in the ionic strength of the solution. Thus, according to the reference data, when the concentration of magnesium chloride is changed from 1 mol/kg H_2O to 5 mol/kg H_2O, the average ionic coefficient of $MgCl_2$ exhibits a more than 20-fold increase from approximately 0.57 to 14. In addition, in the course of a quantitative analysis of such systems, the competing coextraction of the outsalting agent, magnesium chloride in this experiment, should be considered.

Confirming of the influence of the latter factor, Fig. 3 shows an isotherm of magnesium chloride extraction using a mixture of TBP with molecular iodine (*1*) and TBP without iodine (*2*).

The results show that the addition of iodine to the organic phase significantly enhances the extraction of this outsalting agent, alongside with scandium. It should be also noted that as the organic phase is satu-
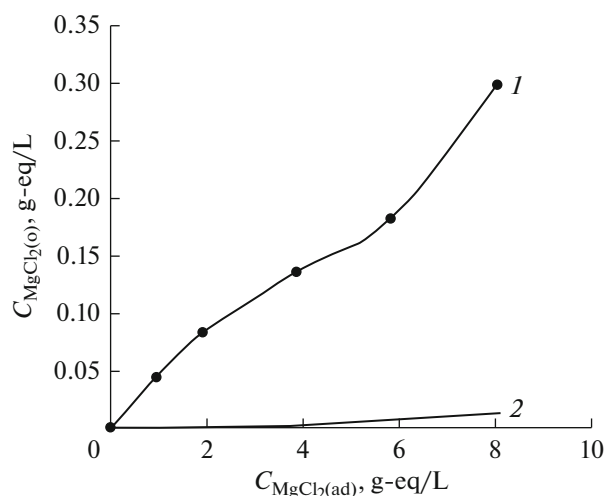
Fig. 3. Isotherm of of magnesium chloride extraction by 80% TBP in toluene: (*1*) in the presence of 0.2 mol/L iodine in the organic phase; (*2*) without iodine.

Fig. 4. Scandium distribution coefficients depending on TBP concentration: initial aqueous solution—$C_{MgCl_2} = 3.5$ mol/L; $C_{ScCl_3} = 0.01$ mol/L; initial organic solution—$C_{I_2} = 0.2$ mol/L; $C_{TBP} = $ var.

rated with magnesium chloride, the ratio between the content of the extracted chloride ion in the complex salt significantly (1.5 times) exceeds the iodine content. In this case, the nature of the isotherm indicates the saturation of the organic phase with magnesium chloride is not achieved. This result can be explained by the formation of mixed salts such as $MgCl(ClI_2) \cdot pL$ nominally formed by HCl and a complex acid $H[ClI_2]$ in the organic phase when it is saturated with magnesium chloride.

The coextraction of the outsalting agent significantly complicates the quantitative description of the system, considering, in addition, a possible interaction of extracted compounds between each other.

Figure 4 shows an effect of TBP concentration on the scandium distribution coefficients. The curve has a complex *S*-shaped character and exhibits an increase in the slope ratio with increasing TBP concentration in the initial part of the curve, and a decrease with high TBP concentration. The quantitative analysis thereof also requires consideration of the competing extraction of magnesium chloride.

Selectivity is one of the most important extraction parameters. To assess the selectivity of scandium extraction, the system under study should be compared with the extraction of different metal salts from a mixture of their chlorides in the presence of ammonium chloride. An 80%-solution of TBP in toluene has been used as the extractant at different concentrations of iodine in the organic phase. The content of metal chlorides in the initial aqueous solution was 0.002 mol/L, and that of ammonium chloride was 5.6 mol/L. The choice of ammonium chloride as an
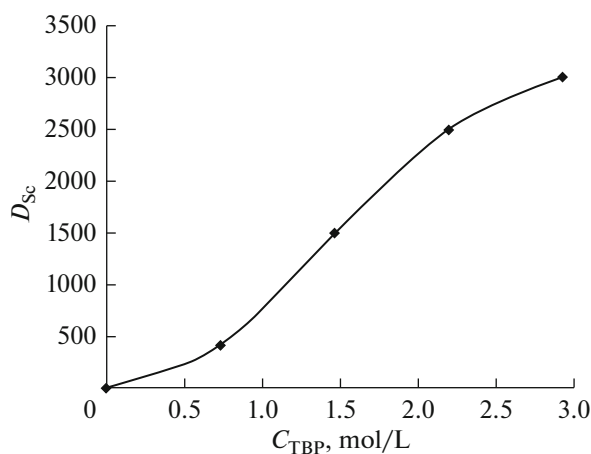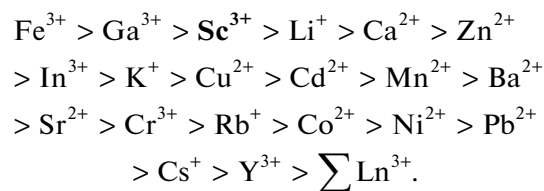
outsalting agent is due to a high purity of the salt and by the most favorable conditions for the analysis of solutions by means of mass spectrometry with inductively coupled plasma. The reextraction of salts from the organic phase was carried out using water acidified to pH 2.5 with hydrochloric acid (to prevent the hydrolysis of metals and to improve the delamination of phases) after a 10-fold dilution of the organic phase.

The results of semiquantitative analysis (determination error ranging from 5 to 30%) as a change in the distribution coefficients of metals depending on the concentration of molecular iodine in the organic phase are shown in Fig. 5. As may be seen, iodine additives exert the greatest effect on the extraction of scandium and lithium chlorides. According to the value of the distribution coefficients for an 80% TBP solution of in the presence of 0.3 mol/L of iodine, the metals can be arranged in the following series:

$$Fe^{3+} > Ga^{3+} > \mathbf{Sc^{3+}} > Li^+ > Ca^{2+} > Zn^{2+}$$
$$> In^{3+} > K^+ > Cu^{2+} > Cd^{2+} > Mn^{2+} > Ba^{2+}$$
$$> Sr^{2+} > Cr^{3+} > Rb^+ > Co^{2+} > Ni^{2+} > Pb^{2+}$$
$$> Cs^+ > Y^{3+} > \sum Ln^{3+}.$$

Scandium can be extracted from a complicated mixture of alkali, alkaline-earth, rare and nonferrous metals by means of the extractant under study in a most efficient way, being somewhat inferior only to iron (3+) and gallium (3+). As far as the latter elements are concerned, the iodine additives barely affect the values of the distribution coefficients, which indicates a direct extraction of these metals by TBP in the
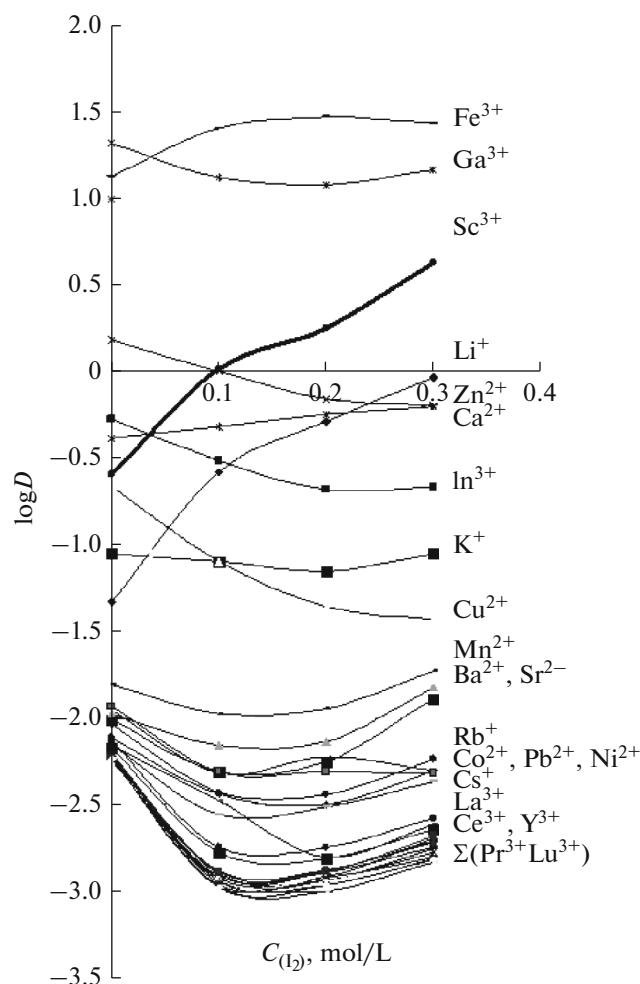
Fig. 5. The values of $\log D_{Mi}$ depending on the concentration of molecular iodine in the organic phase in the course of the extraction of chlorides of different metals using TBP solutions: organic phase—$C_{TBP} = 80\%$ (in toluene); $C_{I_2} =$ var; aqueous phase—$C_{NH_4Cl(ini)} = 5.6$ mol/L; $C_{MCl_i(ini)} = 0.002$ mol/L (for each element).

phase and to operate using such equipment that protects the organic phase from intense illumination.

CONCLUSIONS

Studies on the extraction of scandium from chloride solutions using TBP and molecular iodine mixtures have been carried out. It has been found that iodine additives significantly enhance the extraction of scandium by tributyl phosphate, apparently, owing to the formation of hydrophobic $C1I_2^-$ anions, which are a part of the extractable scandium complexes. The metal distribution coefficients exhibit an increase with increasing TBP and iodine concentration in the organic phase, and with increasing chloride-ion concentration in the aqueous phase. As an outsalting agent, chlorides of alkali, alkaline earth and other weakly extracted metal cations can be used. From the organic phase, scandium chloride can be readily reextracted with water.

In a series of 34 metals, the scandium in the studied system yields only to iron (3+) and gallium (3+) in extractability, which creates broad prospects for the practical use of the process for extracting scandium from hydrochloric-acid leaching solutions of scandium-containing minerals.

REFERENCES

1. Bykhovskii, L.Z., Real, potential, and promising sources of rare-earth raw materials in Russia, *Miner. Resur. Ross., Ekon. Upr.*, 2014, no. 4, pp. 2–8.

2. Favorskaya, L.V., Koshul'ko, L.P., and Presnetsova, V.A., *Tekhnologiya mineral'nogo syr'ya* (The Technology of Mineral Raw Materials), Alma-Ata: Kaz. IMS, 1975, no. 2, pp. 67–72.

3. Gorokhov, D.S., Poponin, N.A., Kukushkin, Yu.M., and Kazantsev, V.P., RF Patent 2417267, 2011.

4. Zlobina, Ye. and Pak, L., Application of binary extractants of scandium, *Chem. Bull. Kaz. Natl. Univ.*, 2013, no. 4, pp. 168–176. https://doi.org/10.15328/chem-b_2013_4168-176

5. Korovin, S.S., Glubokov, Yu.M., Petrov, K.I., et al., Interaction of metal chlorides with organophosphorus compounds, in *Khimiya protsessov ekstraktsii* (The Chemistry of Extraction Processes), Moscow: Nauka, 1972, pp. 162–171.

6. Favorskaya, L.V., Presnetsova, V.A., Vainberger, G.N., et al., *Tekhnologiya mineral'nogo syr'ya* (The Technology of Mineral Raw Materials), Alma-Ata: Kaz. IMS, 1972, no. 2, pp. 173–178.

7. Lebedev, V.N., Extraction and refining of scandium upon the processing of baddeleyite concentrates, *Theor. Found. Chem. Eng.*, 2007, vol. 41, no. 5, pp. 718–722. https://doi.org/10.1134/S0040579507050466.

8. Tatsuya, S., Takeshi, H., and Mitsuo, S., Studies of scandium in various solutions. II. The extraction of scandium(III) with tributyl phosphate from perchlorate-chloride and perchlorate-nitrate media, *Bull.*

form of $FeCl_3$ and $GaCl_3$ or such complex salts as NH_4FeCl_4 and NH_4GaCl_4.

A high selectivity of scandium chloride extraction using TBP and molecular iodine mixtures presents good prospects for using this process to extract scandium from hydrochloric-acid leaching solutions of scandium-containing raw materials. When using this system in practice, it is necessary to bear in mind the highly corrosive action of TBP and iodine mixtures, which is required for making extraction reactors of titanium or plastics (polypropylene, polyethylene) resistant to molecular iodine. In addition, to avoid the iodization of hydrocarbon diluents and iodine loss, which occurs to a considerable extent, for example, in the case of kerosene under illumination, saturated hydrocarbons should be used to dilute the organic

Chem. Soc. Jpn., 1966, vol. 39, no. 2, pp. 244–246. https://doi.org/10.1246/bcsj.39.244.

9. Samoilov, Yu.M. and Isupov, V.P., RF Patent 2081831, 1997.

10. Sokolov, A.B. and Zolotov, Yu.A., *Vliyanie indiya na ekstraktsiyu mikroelementov iz bromidnykh rastvorov* (Effect of Indium on the Extraction of Microelements from Bromide Solutions), Obninsk: FEI, 1971.

11. Kuz'min, V.I. and Kuz'mina, A.A., RF Patent 2590550, *Byull. Izobret.*, 2016, no. 19.

12. Korostelev, P.P., *Fotometricheskii i kompleksometrich-eskii analiz v metallurgii* (Photometric and Complexometric Analysis in Metallurgy), Moscow: Metallurgiya, 1984.

13. Vdovenko, V.M. and Bulyanitsa, L.S., On the distribution of cesium iodide between aqueous solutions and iodine solutions in tributyl phosphate, *Radiokhimiya*, 1964, no. 4, pp. 399–404.

14. Kuz'min, V.I., Kuz'mina, V.N., Pashkov, G.L., Ustyuzhanina, N.V., and Rasputin, S.N., Estimating the possibility of the recovery of valuable elements from underground chloride–calcium brines of the Siberian platform, *Sb. statei Rossiisko-indiiskogo simpoziuma "Metallurgiya tsvetnykh i redkikh metallov"* (The Russian–Indian Symposium "Metallurgy of Non-Ferrous and Rare Metals": Collection of Papers), Moscow, 2002, pp. 246–254.

15. Kuz'min, V.I., Kuz'mina, V.N., and Ustyuzhanina, N.V., Extraction of calcium bromide from chloride brines with mixtures of molecular iodine and tributyl phosphate, *Sb. materialov konferentsii "50 let Rossiiskoi ekstraktsii". Nedelya khimicheskikh tekhnologii* (Proc. Conference "50 Years of Russian Extraction": The Week of Chemical Engineering), St. Petersburg, 2002, pp. 121–125.

Translated by O. Polyakov