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CHEMISTRY AND TECHNOLOGY OF RARE,  
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## Obtaining Solid Extractants Based on Mixtures of Tributylphosphate and Molecular Iodine and Researching the Extraction of Scandium from Chloride Solutions

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**Abstract**—SOLEX, a solid extractant for extracting metal chlorides from solutions, has been obtained by impregnating tributyl phosphate (TBP) and iodine into granulated macroporous polystyrene stitched by divinylbenzene. The sorption properties of the product are studied. The possibility of selectively extracting scandium from chloride solutions and its desorption by water are shown. This sorbent can be used for separation from REM. The value of separation coefficients of scandium/REM exceeds 1000.

**Keywords:** sorption, SOLEX, scandium, chloride solutions, tributyl phosphate, iodine

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### INTRODUCTION

The extraction of scandium from solutions of various compositions has been studied well enough. Different technological processes using industrially available extractants and sorbents for solving various problems have been suggested. However, the high costs of extracting this metal from natural or manmade raw materials, conditioned by its low content, require an enhancement of the processes and a search for new technological solutions.

Earlier, the authors have suggested and researched the process of extracting scandium from chloride solutions by a mixture of tributyl phosphate (TBP) and molecular iodine [1–3]. The use of TBP for this purpose is well-known. The process is quite selective; however, the value of coefficients of distribution of scandium by this extractant is low. Different authors have established the possibility of significantly increasing the extraction of scandium in the presence of large low-hydrated anions such as perchlorate ion or

$\text{FeCl}_4^-$  [4] in the solution. The same effect is achieved when using the mixture of technical TBP with iodine as well, which is conditioned by the formation of a hydrophobic anion complex and the extraction of scandium in the form of a complex salt  $[\text{ScCl}_2L_p]^+(\text{ClI}_2)^-$  [3] (where  $L$  is tributyl phosphate and  $p$  is the solvate number). At the same time, iodine remains in the organic phase in the processes of extraction–reextraction, and the extraction of scandium does not require the expended reactants. The

extractant is distinguished by high selectivity to scandium, especially with respect to REM. The extraction is achieved in the presence of desalters—chlorides of weakly extractable metals—and reextraction is achieved by water.

Since the content of scandium in technological solutions is very small, it is reasonable to use sorbents or resins impregnated by extractants, known as resins of levekstrel type or SOLEXs—solid extractants, in such conditions.

The extraction of scandium using various SOLEXs containing TBP and other neutral phosphor-organic extractants (dioctylmethylphosphonium (DiOMP) and different radical phosphine oxide, (DRPO)) has been studied in numerous works [5–8].

Scandium extraction indexes in these systems are similar to extraction. By sorption capability, the reactants are arranged in the series SOLEX-TBP < SOLEX-DiOMP < SOLEX-DRPO, and extraction increases with growth of concentration of hydrochloric acid.

In this work, conditions of obtaining such sorbents based on TBP and iodine are considered and data on sorption of scandium chloride including separation of it from REM are presented.

### EXPERIMENTAL

We used technical TBP, granulated macroporous polystyrene stitched by divinyl benzene (sorbent MN202 Purolite), as well as iodine and other chemical

reactants of qualification CP and AR in this work. The acquisition of SOLEX is presented in the Results and Discussion.

Scandium chloride was sorbed in static conditions by contacting solutions with the sorbent at 25°C.

To determine the concentrations of salts in the sorbent, they were primarily desorbed by water. The concentration of scandium in solutions was determined by the spectrophotometric method using alizarine C.

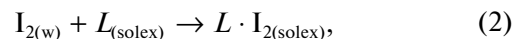
In the presence of other metals, the solutions were analyzed using atomic absorption (an Analyst 400 PerkinElmer spectrometer) or mass spectrometry (ICP-MS Agilent 7500A). The content of  $\text{Cl}^-$  was determined by the argentometric titration of water solutions with potassium chromate as an indicator.

## RESULTS AND DISCUSSION

### *Obtaining SOLEX Based on Mixtures of TBP and Molecular Iodine*

SOLEX was prepared based on granulated macroporous polystyrene stitched by divinyl benzene (sorbent MN202 Purolite). The sorbent was prepared by its sequential saturation firstly by TBP and then by molecular iodine in water. Since the initial sorbent contains a large enough amount of water (humidity constituted up to 57%), it was primarily dried at 50–60°C until reaching a constant weight. It was established that, at the next contact of sorbent saturated by 100% TBP and iodine with water chloride solutions, the partial delamination of the organic phase from polymer matrix is observed. The phase instability of the given system can be caused by the electrolytic dissociation of complex salts formed during sorption [3], which in particular leads to the formation of the third phase upon extraction using saturated hydrocarbons. In order to prevent this phenomenon, the concentration of TBP in the sorbent phase was decreased. For this purpose, the polymer matrix was impregnated by TBP solutions in heptane at various concentrations. Then the sorbent was separated from the excess of the organic solution and heptane was removed by heating (50–60°C) up to a constant weight of the solid product. Phase stability of the sorbent saturated by iodine upon contact with water solutions was achieved at a mass content of TBP in the sorbent of no less than 70%.

The sorbent was saturated by iodine by mixing with molecular iodine in water in the presence of  $\text{HIO}_3$  and sulfuric acid. Additions of small amounts of  $\text{HIO}_3$  (up to 0.002 mol/L) into water solutions were used in this and other experiments in order to eliminate the interfering influence of admixtures of iodide ions in the system, which may be formed as a result of reactions of iodine with admixtures of reducers. Due to limitations of solubility of iodine in water, the process of iodine transfer into the sorbent phase (SOLEX) is split into two stages:



here, indices “sol”, “w”, and “solex” mean the components belong to solid, water, or SOLEX phases, correspondingly;  $L$  is TBP.

It was found that this heterogeneous equilibrium in the system is established quite quickly (20–30 min), which is not typical for sorption and is conditioned by the specificity of extraction of substances by SOLEX, which are closer by their nature to extraction than to sorption. Taking kinetic data into account, the isotherm of interphase distribution of molecular iodine for a polymer sorbent impregnated by TBP (the content of 65%) was obtained. The dependence in the form of mole concentration of iodine in the sorbent phase ( $C_{\text{I}_{2(\text{solex})}}$ ) on its mole concentration in the water phase ( $C_{\text{I}_{2(\text{w})}}$ ) is presented in Fig. 1. It is close to linear. Some deviation from linearity at a high content of iodine is conditioned by a decrease in the active concentration of TBP upon the saturation of the sorbent by iodine at the expense of reaction (2). It can be seen from the above data that iodine distribution coefficients in this system are high and constitute a value of ~5000, which provides low losses of iodine with water solutions upon the operation of the sorbent. In the presence of metal chlorides, losses of iodine significantly decrease at the expense of its combination into hydrophobic chloride complex compounds in organic phase. In contrast to extraction systems, for SOLEX, the concentration of iodine in the sorbent can be raised to maximal values (1 mol/kg and higher), and this does not complicate practical use of the process. There are problems with the separation of phases during extraction at increased concentrations of iodine, when the density of organic phase becomes close to that of water.

### *Researching the Sorption of Scandium Chloride by SOLEX Based on TBP and Iodine*

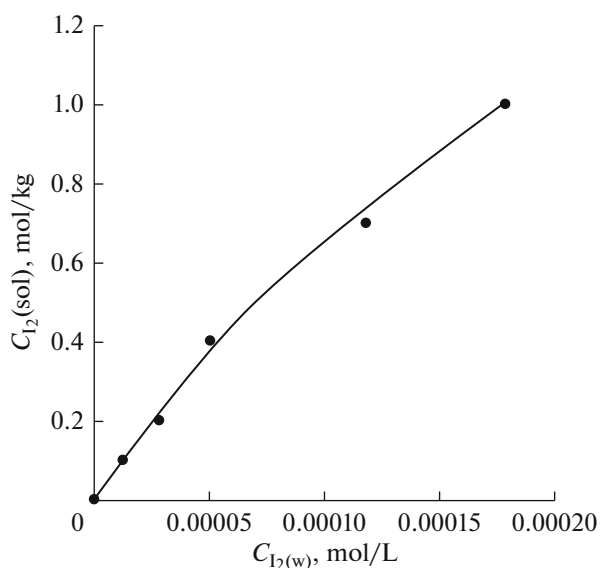
As in the previous case, interphase equilibrium during the extraction of scandium chloride in the researched system is established quite quickly – less than in 1 h – upon saturation of the sorbent by iodine.

Expectedly, the chemical mechanism of the sorption of scandium chloride will be significantly different from the earlier studied extraction system with TBP and iodine [3].

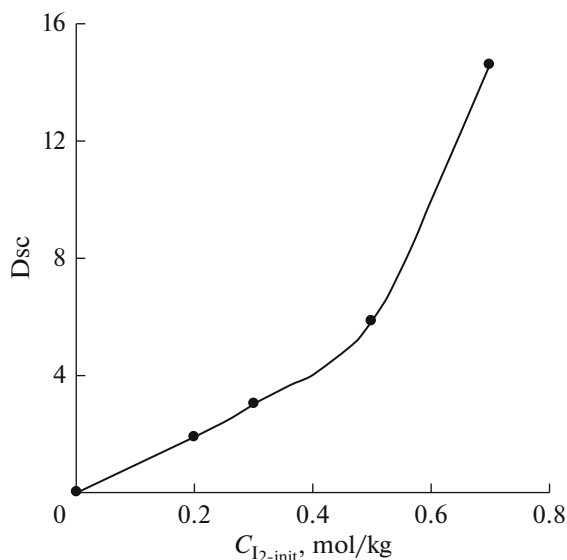
At the same time, the thermodynamic parameters of the processes can be slightly different due to the different nature of the solvent.

In this way, liquid hydrocarbons were used upon extraction, and in SOLEX they were replaced by a polymer matrix.

Similarly to extraction, the interphase sorption reaction was represented in the form of Eq. (3)

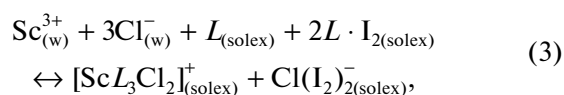


**Fig. 1.** Isotherm of sorption of molecular iodine by the SOLEX-TBP sorbent ( $C_{\text{TBP}} = 65\%$ ). Water solution:  $C_{\text{H}_2\text{SO}_4} = 0.01$  mol/L,  $C_{\text{HIO}_3} = 0.002$  mol/L, and  $\text{I}_2 \sim \text{var}$ ; contact time of phases 1 h.



**Fig. 2.** Dependence of scandium distribution coefficient  $D_{\text{Sc}}$  on the initial concentration of molecular iodine in sorbent  $C_{\text{I}_2\text{-init}}$  upon the extraction by the SOLEX-TBP–iodine sorbent from solutions of lanthanum chloride. Water solution:  $C_{\text{ScCl}_3(\text{init})} = 0.02$  mol/L,  $C_{\text{LaCl}_3(\text{init})} = 1$  mol/L,  $C_{\text{HIO}_3(\text{w})} = 0.002$  mol/L, and  $C_{\text{H}_2\text{SO}_4(\text{w})} = 0.01$  mol/L; ratio S : L = 1 : 5; contact time of phases 1 h.

accounting for the ionic dissociation of the extracted product in the sorbent phase and the formation of a dissolvate— $\text{Cl}(\text{I}_2)_2^-$  and concentration equilibrium constant ( $C_{\text{TM}}$ ) in the form of Eq. (4):



$$C_e = \frac{C_{\text{Sc}(\text{solex})} \cdot C_{[\text{Cl}(\text{I}_2)_2]_{(\text{solex})}^-}}{C_{\text{Sc}(\text{w})} \cdot C_{\text{Cl}(\text{w})}^3 \cdot C_{L(\text{solex})} \cdot C_{\text{I}_2(\text{solex})}^2}, \quad (4)$$

where  $C_{\text{Sc}(\text{w})}$ ,  $C_{\text{Cl}(\text{w})}$ ,  $C_{L(\text{solex})}$ ,  $C_{\text{I}_2(\text{solex})}$ ,  $C_{\text{Sc}(\text{solex})}$ , and  $C_{[\text{Cl}(\text{I}_2)_2]_{(\text{solex})}^-}$  are molar concentrations of the components of reaction (3) in equilibrium water phase and sorbent.

The influence of concentration parameters on sorption equilibrium was analyzed and the correspondence of the data to this reaction was estimated.

When estimating the influence of concentration factors on the sorption equilibrium, lanthanum chloride was used as a desalter. On one hand, this choice is conditioned by the practical importance of the problem of separating scandium from REM and, on the other, by the low extraction of REM chlorides including lanthanum, a mixture of TBP, and iodine [2].

Expression (4) for the equilibrium constant implies the dependence of the value of scandium distribution coefficients ( $D_{\text{Sc}}$ ) on the concentration of the component of the system:

$$D_{\text{Sc}} = \frac{C_{\text{Sc}(\text{solex})}}{C_{\text{Sc}(\text{w})}} = \frac{C_e \cdot C_{\text{Cl}(\text{w})}^3 \cdot C_{L(\text{solex})} \cdot C_{\text{I}_2(\text{solex})}^2}{C_{[\text{Cl}(\text{I}_2)_2]_{(\text{solex})}^-}}. \quad (5)$$

Figure 2 present the dependence of scandium chloride distribution coefficients upon its extraction from solutions of lanthanum chloride on the concentration of iodine in the sorbent.

It can be seen that introducing iodine into the sorbent phase significantly modifies its properties. If in the absence of iodine  $D_{\text{Sc}}$  constitutes about 0.01, then at a concentration of 0.7 mol/kg it increases 1500 times and constitutes 15.

For a semiquantitative estimation of the correspondence of the influence of this parameter to equation of sorption equilibrium (3), let us accept that concentrations of scandium and anion of form  $\text{Cl}(\text{I}_2)_2^-$  in the sorbent phase are approximately equal, i.e.  $C_{[\text{Cl}(\text{I}_2)_2]_{(\text{solex})}^-} \approx C_{\text{Sc}(\text{solex})}$ .

Correspondingly, let us transform Eq. (5) as follows:

$$D_{\text{Sc}} \approx (C_e \cdot C_{\text{Cl}(\text{w})}^3 \cdot C_{L(\text{solex})} \cdot C_{\text{I}_2(\text{solex})}^2) / C_{\text{Sc}(\text{solex})}$$

and then

$$\begin{aligned}
 D_{Sc} \cdot C_{Sc(\text{solex})} &\approx C_e \cdot C_{Cl^-(w)}^3 \cdot C_{L(\text{solex})} \cdot C_{I_2(\text{solex})}^2, \\
 D_{Sc} \cdot (C_{Sc(\text{solex})}) &\cdot (C_{Sc(w)}/C_{Sc(w)}) \\
 &\approx C_e \cdot C_{Cl^-(w)}^3 \cdot C_{L(\text{solex})} \cdot C_{I_2(\text{solex})}^2, \quad (6) \\
 D_{Sc}^2 \cdot C_{Sc(w)} &\approx C_e \cdot C_{Cl^-(w)} \cdot C_{L(\text{solex})} \cdot C_{I_2(\text{solex})}^2, \\
 D_{Sc} \cdot C_{Sc(w)}^{0.5} &\approx (C_e \cdot C_{Cl^-(w)}^3 \cdot C_{L(\text{solex})})^{0.5} \cdot C_{I_2(\text{solex})}.
 \end{aligned}$$

In conditions of this experiment, quantities  $C_{Cl^-(w)}$  and  $C_{L(\text{solex})}$  changed negligibly. For this case, the dependence  $D_{Sc} \cdot C_{Sc(w)}^{0.5}$  on equilibrium concentration of iodine in the sorbent phase (6) must be linear.

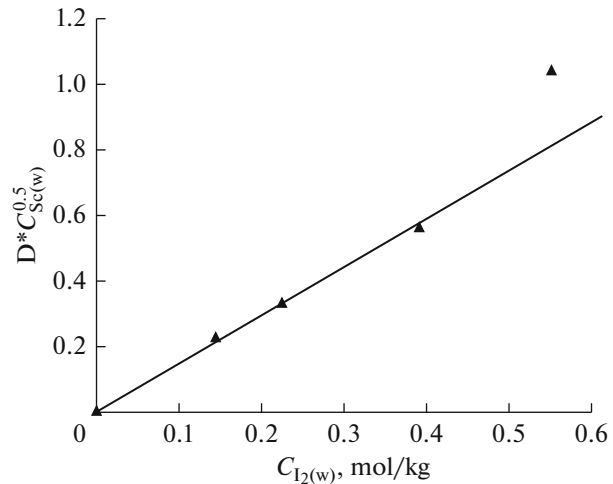
Figure 3 presents data on the extraction of scandium in these coordinates. The dependence is really quite close to linear, according to the assumed main reaction of sorption of scandium chloride. The equilibrium concentration of iodine in the sorbent phase was computed under the assumption of the formation of the dissolvate complex of scandium chloride with iodine.

It is necessary to note that, in the domain of low concentrations of iodine in the organic phase, fewer iodine-solvated anion complexes with  $Cl(I_2)^-$  can be formed, as was established earlier for extracts of scandium chloride by data from the change in their electric conductivity. On the contrary, in the domain of very high iodine concentrations, the degree of solvation of the extracted compounds by iodine can be increased at the expense of the solvation of chloride-ions of the inner coordination sphere of the complex, which was discovered upon the extraction of scandium bromides and iodides.

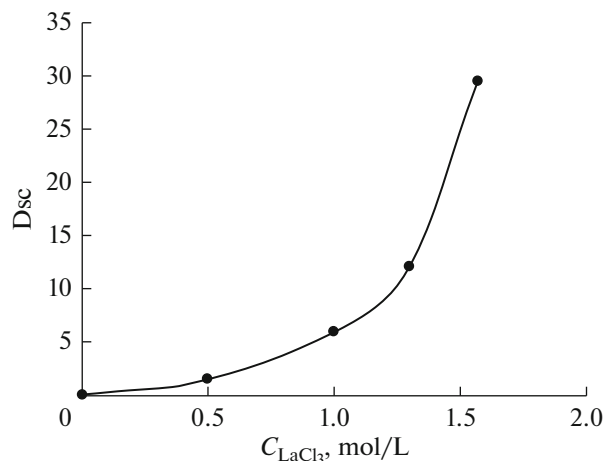
For sorption reaction (3), the value of scandium distribution coefficients is mainly determined by the activity of chloride-ion in water phase. Thus, its increment due to the desalter leads to a growth in the metal extraction, and decrement, on the contrary, leads to decreased extraction, which provides the possibility of desorption of lanthanum chloride, the extraction of which is several orders of magnitude lower than for scandium. According to the expression for the equilibrium constant of the process, the obtained dependence has a power-law character. The value of scandium SOLEX distribution coefficients from this chloride solution reaches 30 at a content of chloride-ion of about 5 mol-eq/L (1.6 mol/L by  $LaCl_3$ ).

It can be easily shown that, at a constancy of concentrations of  $C_{L(\text{sol})}$  and  $C_{I_2(\text{sol})}$ , which is achieved at small amounts of metal, distribution coefficients of scandium will be connected with the activity of chloride-ion in water solution by relation

$$\begin{aligned}
 \log D_{Sc} + 1/2 \log C_{Sc(w)-\text{init}} &\quad (7) \\
 = [1/2 \log(C \cdot C_{L(\text{sol})}) + \log C_{I_2(\text{sol})}] &+ 1.5 \log(C_{Cl^-} \cdot \gamma_{\pm}), \\
 \log D_{Sc} + 1/2 \log C_{Sc(w)-\text{init}} &\approx \text{const} + 1.5 \log(C_{Cl^-} \cdot \gamma_{\pm}).
 \end{aligned}$$

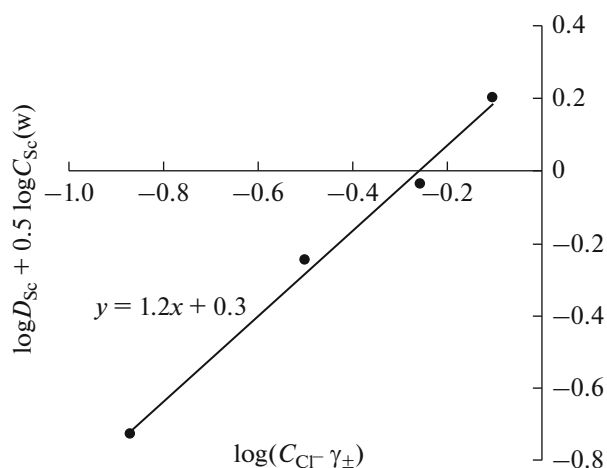


**Fig. 3.** Dependence of quantity  $D_{Sc} \cdot (C_{Sc(w)})^{0.5}$  on the equilibrium concentration of iodine  $C_{I_2}$  upon the extraction of scandium chloride by the SOLEX-TBP–iodine sorbent. Water solution:  $C_{ScCl_3(\text{init})} = 0.02$  mol/L,  $C_{HIO_3(w)} = 0.002$  mol/L, and  $C_{H_2SO_4(w)} = 0.01$  mol/L; ratio S : L = 1 : 5; contact time of phases 1 h.



**Fig. 4.** Dependence of the coefficient of distribution of scandium upon extraction by the SOLEX-TBP–iodine sorbent on the concentration of  $LaCl_3$  in a water solution. Water solution:  $C_{ScCl_3(\text{init})} = 0.02$  mol/L and  $C_{HIO_3} = 0.002$  mol/L; sorbent:  $C_{I_2(\text{solex})} = 0.5$  mol/kg; contact time of phases 1 h.

The corresponding data are presented in Fig. 5. The obtained dependence of  $[\log D_{Sc} + 1/2 \log C_{Sc(w)-(\text{init})}]$  on  $\log(C_{Cl^-} \cdot \gamma_{\pm})$  is really linear and the tangent of its inclination angle is close to 1.2. The slight deviation from the computed value (1.5) is possibly connected with the inaccuracy of computing the coefficient of activity of chloride-ion in the complicated system (the average-ionic coefficients of the activity of the



**Fig. 5.** Dependence of quantity ( $\log D_{Sc} + 0.5 \log C_{Sc(w)-init}$ ) on  $\log(C_{Cl^-} \gamma_{\pm})$  upon the extraction of scandium by the SOLEX-TBP–iodine sorbent. Water solution:  $C_{ScCl_3 init} = 0.02$  mol/L and  $C_{HIO_3} = 0.002$  mol/L; sorbent:  $C_{I_2(solex)} = 0.5$  mol/kg.

desalter—lanthanum chloride—were used instead), as well as with the negligible extraction of lanthanum chloride.

The sorbent, like the extractant based on TBP and iodine, is distinguished by high selectivity with respect to REM. Thus, its use for extracting scandium from solutions of hydrochloric extraction of rare-earth raw materials is especially promising. The value of coefficients of separation scandium/REM in the given system exceeds 1000.

## CONCLUSIONS

SOLEX based on macroporous polystyrene stitched by divinyl benzene, TBP, and molecular iodine was obtained. The delamination of SOLEX into polymer and organic phases during the sorption extraction of chlorides is observed at a content of TBP in the sorbent of higher than 70%. Losses of iodine with water solutions are insignificant. This sorbent is promising for extracting scandium from chloride solutions of complicated composition. Metal is extracted

highly effectively from water solutions containing desalters—chlorides of weakly sorbed metals; desorption is achieved by treating the sorbent with water. The process flows by heterogeneous reaction with the formation of mixed chloride—ionic complexes. The value of scandium distribution coefficients in the presence of REM salts reaches 30 and the coefficient of separation of scandium/lanthanoids exceeds 1000, which means it is possible to use SOLEX for extracting scandium from solutions and pulps of the hydrochloric extraction of rare-earth raw materials.

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