



Extraction of metal bromides from chloride brines with mixtures of molecular iodine and tributyl phosphate

V.I. Kuzmin*, V.N. Kuzmina, N.V. Gudkova, D.V. Kuzmin

Federal State Budgetary Institution of Science Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Akademgorodok, 50/24, 600036 Krasnoyarsk, Russia



ARTICLE INFO

Keywords:

Natural chloride brines
Bromides extraction
Tributyl phosphate
Iodine
Lithium
Calcium, Scandium

ABSTRACT

The process of recovery by direct extraction of metal bromides from calcium chloride brines using mixtures of molecular iodine with tributyl phosphate has been studied. It was found that iodine significantly increases the recovery of the bromides of alkali and alkaline earth metals due to the formation of hydrophobic iodine complexes with the halide anions. Bromides of calcium and lithium are the most selectively extracted. The extracted complexes significantly dissociate into ions in the organic phase. The extraction of calcium halide over a wide range of its concentration in an aqueous solution results in the extraction of a mixed chloride-bromide salt. This is due to a significant difference in the separation factors for bromide and chloride ions in the interphase exchange reactions for the halide ions of the inner and outer coordination spheres of the extracted complex.

1. Introduction

Earlier, we found that a mixture of tributyl phosphate and molecular iodine is a promising extractant system for scandium recovery from chloride solutions (Kuzmin and Kuzmina, 2017a, 2017b). The presence of iodine in this system results in an increase in the distribution coefficient of scandium chloride due to the formation of hydrophobic complex anions $[ClI_2]^-$ and $[Cl(I_2)_2]^-$. Even more stable complexes are formed between molecular iodine and bromide ions which can be used for selective extraction of bromides from natural waters and brines. This is the subject of this work. The data obtained also provide for a better understanding of the chemistry of the extraction of metal salts, including scandium chloride, in these systems.

Chloride-containing ground waters with a high content of salts of various metals are widespread in East Siberia (Russia). They are a promising source of raw materials for such elements as bromine, iodine and lithium. The brines of the Krasnoyarsk, Yakutia and Irkutsk regions are the most promising for processing, which is due to both a high concentration of useful components and the large reserves of these waters.

The calcium chloride brines of East Siberia are raw materials readily treatable by hydrometallurgical processing. As a rule, they contain little solid suspensions, have an optimum temperature of 15–25 °C, are sufficiently concentrated and, at the same time, do not crystallize with decreasing temperature. Table 1 shows the concentration of the

valuable elements of the calcium chloride brines of the Sukhontunguskoye deposit (Krasnoyarsk Region) which are located at depths of 1–3 km. As seen from these data, in addition to bromine, lithium and iodine, the recovery of rubidium and boron from the brines may also be of practical interest.

Despite their potential, up to now, processing of these brines has not been exploited, because of the problems of heat and power supply and transportation because of the remoteness of the brine deposits from industrialized regions. All this imposes significant restrictions on the choice of one or another processing technology and, in particular, the process should be low-cost with regard to energy and materials.

When processing the brines, the main problem is the separation of alkaline and alkaline earth elements with nearly identical properties and the halide ions. Equally challenging is the selective recovery of the alkaline elements from brines in the presence of an overwhelming excess of alkaline-earth metals. Bromine is one of the most valuable elements containing in the brines. The concentration of this element in the rich brines of Siberia is 2–5 g/L.

According to existing practice, bromide is recovered from solution, in which it is present as the bromide ion (Br^-), by oxidation. The solutions are treated with chlorine followed by bromine recovery. For that, steaming or air blowing techniques, resin ion-exchange or solvent extraction methods, as well as membrane processes can be used. So far, however, the attention of researchers has mainly focused on the oxidation process (Yu et al., 2013; Li et al., 2014; Liu et al., 2012; Zhang

* Corresponding author.

E-mail address: kuzmin_vi@mail.ru (V.I. Kuzmin).

Table 1

The content of valuable elements in the calcium chloride brines of the Sukhotunguskoye deposit (Krasnoyarsk Region).

Element	K	Mg	Br	I	Li	Rb	Sr	B
Concentration, g/L	15–23	9–10	2–5	0.001–0.03	0.1–0.2	0.01–0.028	2–2.5	1–2

The overall mineralization is 350–370 g/L.

et al., 2010; Cai et al., 2010; Zhang et al., 2009; Wang et al., 2004; Zhu and Kou, 2003; Yao et al., 2011).

In order to solve the problem of the delivery of highly toxic chlorine to remote deposits and its storage, it was suggested to produce the reagent on site using electrochemical methods (Kotsupalo et al., 2001). To ensure the safe storage and export of toxic bromine, extraction-electrochemical technology for production of a bromine concentrate or its salts has been proposed (Kuzmin et al., 2008; Kuzmin and Kuzmin, 2009).

Given the challenges of the application of the “chlorine” technologies for Siberian deposits, the development of technologies for direct extraction of bromide salts, widely used in practice, is of considerable interest. At the same time, it becomes possible to produce a bromine product with practically no reagent costs. Of these products, the production of calcium bromide is of most interest. Taking into account the salting out effect of the brine components, a significant concentration of calcium bromide in strip liquors can be achieved in the “extraction-stripping by water” cycles.

In the present work, the process of selective extraction of bromides by mixtures of tributyl phosphate with molecular iodine has been studied.

2. Experimental

2.1. Reagents and materials

Tributyl phosphate (TBP) of technical grade was used in this work. All other reagents used were of chemically pure or analytical grades. Heptane and the dearomatized extraction diluent RED-2, a C₁₁–C₁₆ fraction of the series of *n*-alkanes (Russia), were used as diluents for TBP. For the preparation of iodine-containing extractants, TBP and the organic diluent were pretreated with molecular bromine to decompose any organic reducing agent impurities. To this end, molecular bromine was added to the organic solution to a concentration of about 0.1 mol/L. The solutions were kept for 1–2 h in the dark and then washed with a sodium hydroxide solution (1–2 mol/L) and water.

To prevent the separation of a third phase, dibutylphthalate (DBP) in an amount of up to 20% was added to the organic phase during the extraction.

Investigations on the extraction of the elements were carried out using both synthetic solutions and natural calcium chloride brines from the Sukhotunguskoye deposit (Krasnoyarsk Region) and quarry waters from the diamondiferous kimberlite “Udachnaya” (Yakutia). The composition of the brines is given in Table 2.

2.2. Procedure

The liquid-liquid extraction testwork under static conditions was carried out by mixing of the organic and aqueous phases for 5–10 min

Table 2

The composition of the brines from the Sukhotunguskoye deposit and the Yakutian surface waters all located in Siberia.

Element	Br	Li	I	Na	K	Mg	Ca	Sr	Fe	Cl
Concentration, g/L	Sukhotunguskoye deposit									
	4.9	0.22	0.018	60	20.5	8.6	55	2.40	0.075	220
Concentration, g/L	Kimberlite “Udachnaya” (Yakutia)									
	4.4	0.17	< 0.005	25	12.9	15.8	87	1.5	Trace amounts	210

at 25 °C. The volume ratio of the organic and aqueous phases (O:A) was varied. According to preliminary data, the time required to reach equilibrium was 3–5 min. At the end of the extraction process, the phases were separated, filtered, and then analyzed. The chloride concentration and the sum of the chloride and bromide concentrations were determined by argentometric titration of the aqueous solutions with potassium chromate as the indicator. When analyzing organic solutions, the halides were first stripped with water.

The composition of the solutions was determined using an Agilent ICP-MS 7500C spectrometer (Agilent Technologies, Inc., Japan) and an atomic absorption spectrophotometer Analyst 400 (PerkinElmer, Inc., USA). Electrical conductivity measurements of the organic and aqueous solutions were carried out using a conductivity meter type OK-102/1 (Radelkis, Hungary).

3. Results and discussion

Chlorides and bromides of alkali and alkaline earth metals are poorly recovered by tributyl phosphate. The values of their distribution coefficients are < 0.01, even at high concentrations of halides in the aqueous solution. As we have established, the addition of molecular iodine to TBP leads to a sharp increase in the recovery of halides which increases in the series chloride < bromide < iodide. This order corresponds to an increase in the stability of the complex ions formed $ClI_2^- < BrI_2^- < I_3^-$ and to the growth of hydrophobicity due to an increase in the size of the anions, which contributes to an increase in the extraction. This process is considered in more detail.

3.1. Assessment of the interaction between molecular iodine and TBP and the losses of iodine in the system

Molecular iodine is fairly soluble in organic hydrocarbon solvents but in the presence of TBP, its solubility increases significantly. This is accompanied by noticeable changes in the electronic absorption spectra of the solutions, indicating the formation of a complex of iodine with TBP. Thus, in heptane solution, the maximum absorption of iodine at 540 nm is shifted to 438 nm in the presence of 30% TBP. Similarly, when contacting the organic solutions with water, increasing the concentration of TBP results in an increase in the iodine interfacial distribution coefficients. This dependence is shown in Fig. 1. The data were obtained for water and a dilute solution of sulfuric acid (0.01 mol/L) and heptane as the solvent. The coincidence of the results for both systems indicates that there is no appreciable hydrolysis or disproportionation of iodine in water according to reaction (1).



As seen, the dependence is initially close to linear, while deviating from linearity with an increasing iodine distribution coefficient at a high concentration of TBP. The results can be satisfactorily described by

Download English Version:

<https://daneshyari.com/en/article/6658832>

Download Persian Version:

<https://daneshyari.com/article/6658832>

[Daneshyari.com](https://daneshyari.com)