## INORGANIC SYNTHESIS
## AND INDUSTRIAL INORGANIC CHEMISTRY

# Technology for Joint Production of Bromine and Lithium Bromide from Brines from Siberian Platform

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**Abstract**—Two methods for obtaining bromine and lithium bromide from highly mineralized brines enriched with lithium- and bromine-containing compounds, with Li : Br atomic ratio of 0.4–0.8, were studied. These methods are based on a combination of the technique for production of bromine and sorption recovery of lithium from brines to give eluates, LiCl solutions.

Lithium bromide is an expensive reagent in short supply, which is in high demand in the market of lithium products. The prospects for high demand for this compound is mainly associated with its use in refrigeration engineering and in manufacture of heat pumps.

Most of the existing industrial techniques for manufacture of LiBr are based on the reaction of lithium hydroxide or carbonate with hydrobromic acid [1, 2] or elementary bromine in an aqueous medium in the presence of a reducing agent, e.g., hydrogen peroxide [3] or ammonia [4]. The common shortcoming of these methods is the high cost of LiBr obtained, which is due to the fact that expensive commercial lithium compounds, hydrobromic acid, and liquid bromine are used in the process. At present, HBr and $Br_2$ are manufactured in Russia in limited amounts and mainly from imported raw materials. In this context, development of more economic methods for production of LiBr from new kinds of raw materials is rather a topical task.

As comparatively low-cost and available raw material for production of both liquid $Br_2$ and LiBr can serve highly mineralized brines from the Siberian platform, which contain considerable amounts of compounds of lithium and bromine simultaneously. The lithium to bromine atomic ratio in brines of this type is 0.4–0.8, and, therefore, only part of bromine contained in a brine, rather than its whole amount, is required for obtaining LiBr. The remaining part

can be used to manufacture liquid $Br_2$ as commercial product.

The most promising technique for processing of brines of this kind is that combining two main technological procedures: production of bromine and selective recovery of lithium ions to give lithium products. Of the known industrially used techniques for manufacture of bromine, the best applicable to the case in question is that based on steam induced desorption of elementary bromine after oxidation of bromide ions with chlorine. However, an important shortcoming of this technique is the necessity for use of liquefied chlorine, which is ecologically unsafe and involves difficulties in its transportation, storage, and use. To improve the ecological and economic characteristics of this technique, the authors suggest to oxidize bromide ions with chlorine obtained by anodic oxidation of chlorine ions contained in the brine, rather than with liquefied chlorine. Such a technology, based on electrochemical oxidation of $Br^-$ ions with anodic chlorine, combined with steam-induced desorption of the $Br_2$ formed, is, presumably, the most promising for large-scale manufacture of $Br_2$[1] [5].

A sorption technique based on use of an inorganic lithium-selective sorbent $LiCl \cdot 2Al(OH)_3 \cdot mH_2O$ (DGAL-Cl) has been developed for recovery of lithi-

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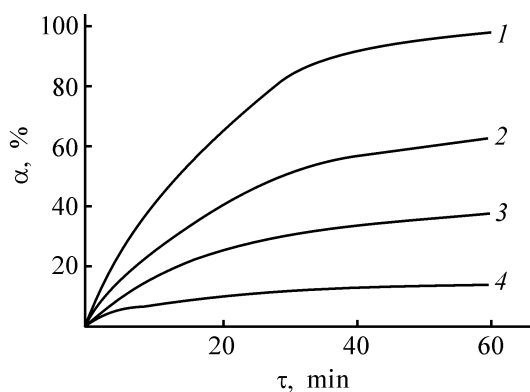[1] For manufacture of $Br_2$ from brines from the Siberian platform.

**Fig. 1.** Kinetic curves for the degree $\alpha$ of bromine absorption by LiOH solution in the presence of a reducing agent from bromine–air mixture with varied content of $Br_2$. ($\tau$) Time. $Br_2$ content $c \times 10^2$ in air (g $l^{-1}$): (*1*) 25.7, (*2*) 16.2, (*3*) 9.7, and (*4*) 3.7.

um ions from highly mineralized brines [6]. In this method, lithium ions are recovered from the brine in the form of a selective-sorption eluate, a dilute LiCl solution with concentration of 7–10 kg m$^{-3}$, which contains a certain admixture of calcium and magnesium compounds removable by an appropriate purification procedure.
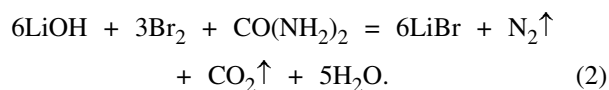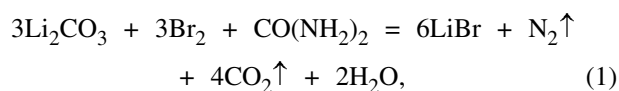
In elaboration of the techniques developed for recovery of lithium and bromine ions from brines of the Znamenskoe deposit (Irkutsk oblast), two new technological procedures were suggested for joint production of LiBr and elementary bromine. The first of these combines a procedure for manufacture of bromine and that for production of LiOH or $Li_2CO_3$ from selective-sorption eluates. A LiOH solution can be obtained by electrochemical conversion of a lithium chloride solution or its mixture with lithium carbonate [7, 8], and $Li_2CO_3$ slurry, by carbonization of a LiOH solution with carbon dioxide. Lithium bromide is obtained by bromination of lithium hydroxide or carbonate. As a brominating agent in the given method serves bromine vapor evolving from bromine water formed in isolation of bromine in the stage of steam desorption [1].

The second variant also includes a technique for production of liquid bromine; however, it is suggested to obtain LiBr directly from selective-sorption eluates (LiCl solutions) by ion exchange in desorption of lithium ions from the cation-exchange resin with a hydrobromic acid solution obtained by reduction of liquid bromine in an aqueous medium. Thus, the aim of this study was to make comparative analysis of the two suggested technological procedures for joint production of $Br_2$ and LiBr from natural brines.

## EXPERIMENTAL

Laboratory studies were carried out with model solutions imitating the composition of a brine[2] with average composition (g $l^{-1}$): LiCl 2.5, NaCl 6.1, KCl 8.2, $MgCl_2$ 115, $CaCl_2$ 335, and $Br^-$ 9.3; Li : Br atomic ratio 0.5. In studying multicomponent systems containing $Br^0$, $Br^-$, and $Cl^-$, analysis of solutions and the gas phase was performed using methods commonly accepted in manufacture of bromine [9]. The content of chloride ions in solutions was determined by mercurimetric titration, and that of calcium and magnesium ions, by trilonometry [10]; lithium ions were analyzed by flame photometry on an SP-9 spectrophotometer [11].

The first technological variant employs bromine water as a brominating agent. To obtain bromine vapor, bromine water was placed in a flask thermostated at 50°C. The flask was connected to absorbing vessels filled, depending on the aim of an experiment, with LiOH solution or $Li_2CO_3$ slurry. Bromine vapor was driven-off from bromine water with air from a compressor, with the content of bromine in the bromine–air mixture varied from 0.04 to 0.26 kg m$^{-3}$. The concentration of the LiOH solution was 50 g $l^{-1}$, the liquid to solid phase ratio (l : s) in the $Li_2CO_3$ slurry was varied from 3 to 11. As a reducing agent was used carbamide, with its amount varied in the range 0.75–1.5 relative to that required by the stoichiometry for reduction of elementary bromine to the bromide ion in accordance with the equations describing the chemical reactions

$$3Li_2CO_3 + 3Br_2 + CO(NH_2)_2 = 6LiBr + N_2\uparrow$$
$$+ 4CO_2\uparrow + 2H_2O, \tag{1}$$

$$6LiOH + 3Br_2 + CO(NH_2)_2 = 6LiBr + N_2\uparrow$$
$$+ CO_2\uparrow + 5H_2O. \tag{2}$$

As is known, the rate of bromine absorption by solutions of alkali or alkali metal carbonates is determined by the resistance of the boundary gas layer [1], being proportional to the bromine concentration in the gas phase. Figure 1 shows kinetic curves for the degree of bromine absorption by a LiOH solution from a bromine–air mixture with varied content of $Br_2$. As would be expected, the process is the faster and the degree of bromine absorption the greater, the higher the bromine concentration in the bromine–air mixture. The isotherm of bromine absorption is linear in the concentration range under study.
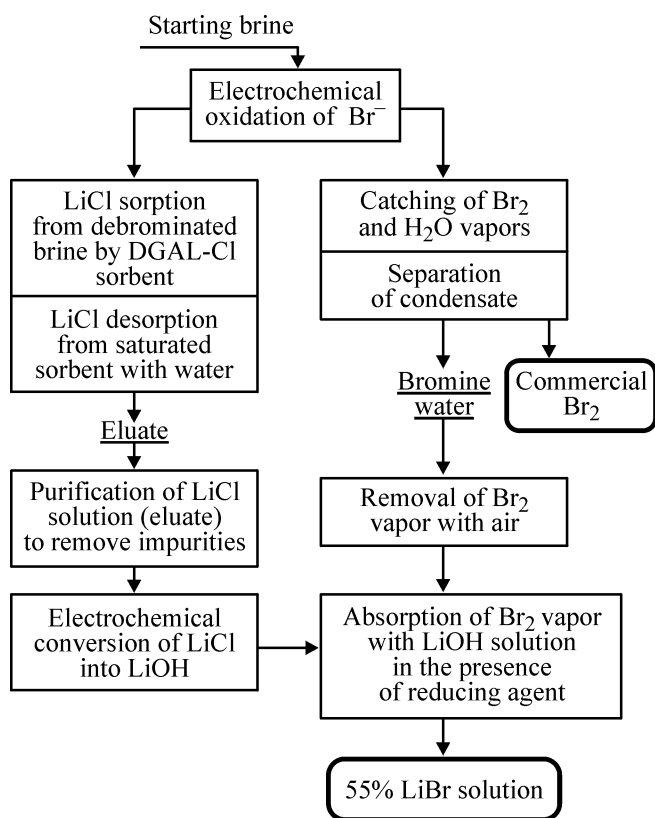
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[2] Znamenskoe deposit (Irkutsk oblast).

With $Li_2CO_3$ slurry used to obtain lithium bromide, it was established that the concentration of the resulting LiBr solution increases with decreasing l : s ratio in the slurry, which is indicated by the data presented below:

| The l : s ratio in slurry | 11 | 7 | 4 | 3 |
|---|---|---|---|---|
| LiBr concentration, g $l^{-1}$ | 125 | 246 | 381 | 440 |

Consequently, the l : s ratio is to be lowered for obtaining more concentrated LiBr solutions.

In the experiments, highly concentrated LiBr solutions with concentration of 400 g $l^{-1}$ and more were obtained from saturated LiOH solutions and $Li_2CO_3$ slurry. In both cases, a certain excess of a reducing agent, about 20% relative to the stoichiometry of reactions (1) and (2), is necessary for more complete absorption of the bromine vapor. On the basis of the studies performed, technological Scheme 1 for obtaining LiBr with bromine vapor used as brominating agent has been developed [12].

Starting brine
↓
Electrochemical oxidation of $Br^-$

LiCl sorption from debrominated brine by DGAL-Cl sorbent
LiCl desorption from saturated sorbent with water
↓
Eluate
↓
Purification of LiCl solution (eluate) to remove impurities
↓
Electrochemical conversion of LiCl into LiOH

Catching of $Br_2$ and $H_2O$ vapors
Separation of condensate
↓
Bromine water — Commercial $Br_2$
↓
Removal of $Br_2$ vapor with air
↓
Absorption of $Br_2$ vapor with LiOH solution in the presence of reducing agent
↓
55% LiBr solution

**Scheme 1.**

The second method for producing LiBr directly from eluates obtained from brine as LiCl solutions is based on sorption of lithium ions by a KU-2×8 cation-exchange resin in the $H^+$ form, with its subsequent
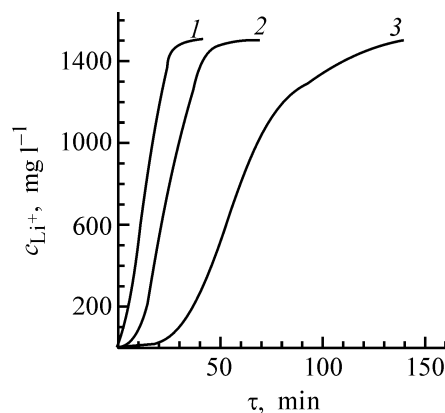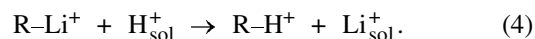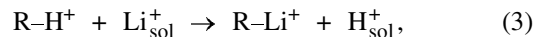


**Fig. 2.** Output curves of lithium ion sorption by KU-2×8 cation-exchange resin at different linear flow velocities of the solution. ($c_{Li^+}$) Concentration of $Li^+$ ions and ($\tau$) time. $W$ (m $h^{-1}$): (1) 26, (2) 15, and (3) 7.4.

desorption with hydrobromic acid to give a LiBr solution. Laboratory studies were carried out with model LiCl solutions in distilled water, with the concentration of lithium ions in the solutions varied from 3 to 1500 mg $l^{-1}$. Sorption was performed at room temperature in a glass column 60 mm high and 1.09 cm in diameter, packed with 50 $cm^3$ of KU-2 × 8 cation-exchange resin at bed height of 54 cm. The kinetics of sorption of lithium ions by the cation-exchange resin was studied by the dynamic method. A solution to be passed through the sorption stage was fed from below upwards by a dosage pump, with the linear flow velocity $W$ of the solution varied from 7.4 to 26 m $h^{-1}$. The cation-exchange resin saturated with lithium ions was washed to remove chloride ions with demineralized water, after which lithium ions were desorbed with a HBr solution. The process in which LiBr is obtained can be described by the following ion-exchange reactions

$$R–H^+ + Li^+_{sol} \rightarrow R–Li^+ + H^+_{sol}, \qquad (3)$$

$$R–Li^+ + H^+_{sol} \rightarrow R–H^+ + Li^+_{sol}. \qquad (4)$$

In the initial stage of dynamic studies, output curves of lithium ion sorption by the cation-exchange resin were obtained at different flow velocities of a LiBr solution with concentration of 9.2 g $l^{-1}$, which corresponded to lithium ion concentration of 1500 mg $l^{-1}$. The dependences obtained (Fig. 2) made it possible to determine the time necessary for complete saturation of the cation-exchange resin and its dynamic exchange capacity (DEC), and to calculate the working zone height $H_{w.z}$ for each case. The sorption was performed in the plug-flow mode, which made it pos-

**Table 1.** Basic parameters of the process of lithium ion sorption by KU-2×8 cationite

| Flow velocity of LiCl solution through cationite, $W$, m h$^{-1}$ | Time elapsed till complete saturation of cationite with Li$^+$, $\tau$, min | DEC, mg-equiv ml$^{-1}$ | $H_{w.z}$, m |
|---|---|---|---|
| 7.4 | 135 | 1.78 | 0.64 |
| 15.0 | 60 | 1.61 | 0.77 |
| 26.0 | 35 | 1.58 | 0.89 |

**Table 2.** Basic technological characteristics of the process of lithium ion desorption from saturated cationite with HBr solutions

| $c_{HBr}$, M | Degree of Li ion desorption, % | Concentration of the resulting LiBr solution, g l$^{-1}$ | Degree of utilization of the desorbing solution, % |
|---|---|---|---|
| 0.7 | 41.0 | 62.5 | 99.2 |
| 1.5 | 72.0 | 129.3 | 99.2 |
| 2.0 | 98.5 | 174.0 | 100 |
| 2.2 | 98.8 | 184.6 | 96.5 |
| 2.5 | 98.9 | 187.2 | 86.1 |

sible to use in the calculations the Michaels–Treible formula [13]:

$$H_{w.z} = H_b \frac{\tau_{eq} - \tau_{br}}{\tau_{eq} - (1 - \phi)(\tau_{eq} - \tau_{br})},$$

where $H_b$ is the height of the fixed bed of the cation-exchange resin (m); $\tau_{eq}$, the time in which a concentration equal to $0.95 c_{in}$ appears after the cationite bed (h); $\tau_{br}$, the time in which a breakthrough concentration equal to $0.05 c_{in}$ appears after the cationite bed (h); $\phi$, the symmetry parameter of the curve.

It was established in the experiments that raising $W$ leads to an increase in $H_{w.z}$, with the dependence being linear. As expected, the capacity characteristics of the cation-exchange resin decrease somewhat, as also does the degree of lithium ion sorption from solutions, with increasing flow rate of the solution. It should be added that the dynamic exchange capacity of the cation-exchange resin in the concentration range of lithium ions in LiCl solutions (3–1500 mg l$^{-1}$), used in this study, remains virtually constant, being equal to 1.6 mg-equiv ml$^{-1}$ (Table 1).

Lithium ions were desorbed from the cationite in three stages with HBr solutions at $1:s = 1:1$ for each stage by Scheme 2 modeling the process of continuous counterflow desorption (horizontal arrows denote the flow of the cation-exchange resin, and vertical arrows, that of the desorbing HBr solution). It was established experimentally that the optimal HBr concentration in the desorbing solutions is 2.0–2.2 M. As can be seen from the data in Table 2, only this concentration ensures the most complete (~99%) re-

covery of lithium ions from the cation-exchange resin and the maximum concentration of LiBr in the final desorbate. Use of more concentrated hydrobromic acid solutions for desorption of lithium ions is inexpedient because of the low extent of their utilization.
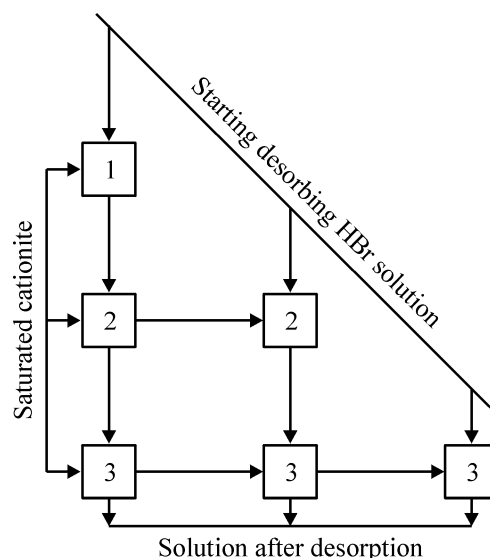


**Scheme 2.**

HBr solutions of required concentration were obtained by reacting elementary bromine with a reducing agent in an aqueous medium. The most appropriate reducing agents for this purpose are hydrazine, carbamide, and their derivatives, which form as a result of a redox reaction inert gaseous substances, $N_2$ and $CO_2$:

$$2Br_2 + N_2H_4 = 4HBr + N_2\uparrow. \qquad (5)$$

The synthesis was carried out at room temperature under conditions of continuous metering-out of liquid bromine and agitation of the reaction mass until its total decoloration, which indicated the completion of the reaction. It was established experimentally that reaction (5) proceeds in strict conformity with the stoichiometry, with no excess of reagents required. This method for obtaining lithium bromide has been patented [14], its technological flowsheet is represented by Scheme 3. A solution of hydrobromic acid was used as brominating agent [14].
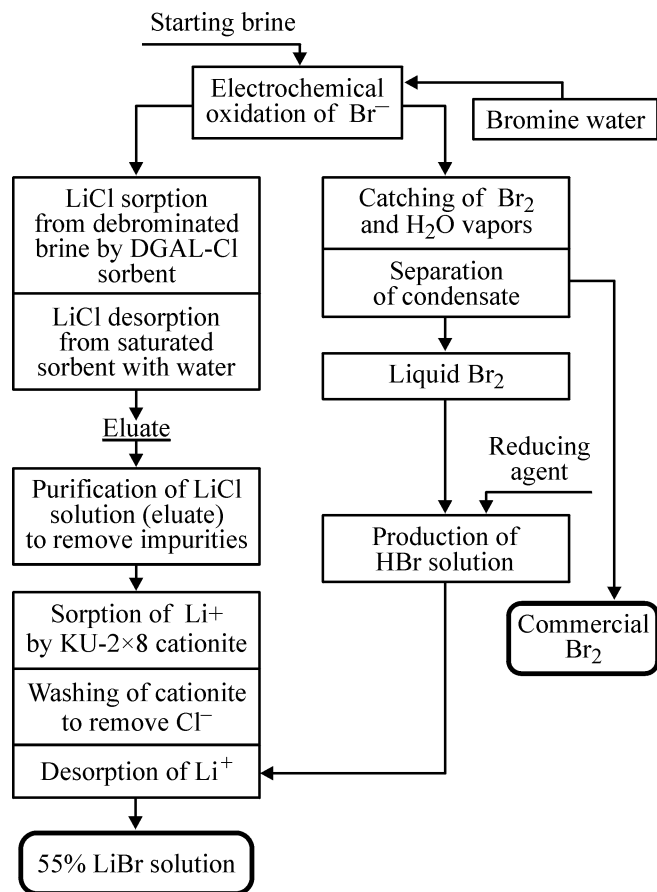


**Scheme 3.**

As already mentioned, both the methods yield two commercial products, $Br_2$ and LiBr, within a single technological scheme. It should be noted that, on the whole, the second method for LiBr manufacture directly from selective-sorption eluates obtained in the initial stages of brine processing is simpler and less expensive than the first technique, which involves power-intensive stages of LiOH or $Li_2CO_3$ production, which require intricate equipment. As for the choice of the optimal method for obtaining LiBr, it is determined by specific features and conditions of a particular production shop being designed or by availability of low-cost $Li_2CO_3$.

Combined schemes for joint production of $Br_2$ and LiBr from brines make it possible to lower substantially the manufacturing cost of the products obtained.

## CONCLUSIONS

(1) Two variants of a technology for joint production of $Br_2$ and LiBr with bromine vapor or hydrobromic acid as brominating agents were developed.

(2) The second technique, which does not require additional expenditure for conversion of LiCl into LiOH or $Li_2CO_3$ for catching of bromine vapor, is simpler and less expensive.

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