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Abstract

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Isotripolyhalides of Alkali Elements Similar in Properties and Their Application for Purifying Rubidium Compounds from Cesium

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The successes achieved very recently in solving the problem of separating alkali elements similar in properties are, to a considerable extent, associated with the use of their polyhalides ([1-5]). Thus, as a result of applying the method of double precipitation of rubidium chlorobromoiodate of composition $Rb[J(ClBr)] \cdot H_2O$, a method was developed ([1,2]) for purifying technical rubidium salts from potassium, with the production of especially pure preparations of this element containing only 0.0002% potassium. Subsequently, ([3]) a technological scheme was outlined for deep purification of RbCl through rubidium chlorobromoiodate. In this way the most difficult task of removing a potassium microimpurity from rubidium salts was solved; moreover, since a compound of the type $Me[J(ClBr)]$ exists only for cesium, precipitation of $Rb[J(ClBr)] \cdot H_2O$ achieves purification of rubidium salts from all alkali elements except cesium.

With the aid of cesium diiodobromide $CsBrJ_2$, the problem of removing a rubidium microimpurity from cesium salts was solved. The use of $CsBrJ_2$ makes it possible to purify cesium salts also from all other alkali elements, since in the series of their compounds $CsBrJ_2$ is the only one with the anion BrJ_2^-. Already a double precipitation of $CsBrJ_2$ makes it possible ([4,5]), from technical CsBr containing 5% rubidium and 1.5% of the remaining alkali elements, to obtain a product with an impurity content of not more than 0.05%, including 0.02% rubidium. The high purification factor (10-20) and selectivity of extracting CsBr from a mixture with other alkali elements give the method substantial advantages over those proposed earlier. Two further recrystallizations of $CsBrJ_2$ make it possible to obtain CsBr containing not more than 0.0003-0.0005% rubidium, i.e., such cesium compounds as cannot yet be obtained by any of the other known methods.

The successful solution of the most difficult problem of removing a potassium microimpurity from rubidium salts and the development of a method for removing microimpurities of all alkali elements from cesium salts brought to the fore the question of solving a similar general problem as applied to rubidium compounds. Along this path it remained to overcome difficulties associated

with the separation of rubidium and cesium (removal of a microimpurity of the latter). Experience in the application of polyhalides of alkali elements similar in properties showed that they may also be useful for work in the indicated direction.

However, the above-mentioned achievements in obtaining pure rubidium and cesium compounds are associated with the use of heteropolyhalides, in particular heterotripolyhalides ([5]), among which there are no compounds that would make it possible to free rubidium salts from a cesium microimpurity. Therefore our attention was directed to another group of polyhalides—isopolyhalides. For alkali elements similar in properties, polybromides ($MeBr_3$) and polyiodides (MeJ_3) are known; moreover, for polybromides the existence of only tribro-

cesium (6-9) and rubidium (10,11). Cesium tribromide can be isolated both from solution (6-8) and obtained by a dry method (9). Rubidium tribromide is isolated from aqueous solutions under conditions analogous to those for obtaining cesium tribromide. At the same time, solid potassium tribromide of composition KBr_3 has not been isolated, and only the existence (12,13) of the crystalline hydrate $KBr_6 \cdot 1.5H_2O$ is known. Thus, polybromides could be used at most for purifying rubidium and cesium salts from other cations, but not from one another. Moreover, rubidium and cesium polybromides partially decompose upon recrystallization from water (6,10,14).

Polyiodides are more stable, in particular cesium triiodides (6,15-18) and rubidium triiodides (10,17,19), which can be isolated from solutions and recrystallized from water. It is characteristic here that the solubility of CsJ_3 is 300 times lower (10) than the solubility of RbJ_3. This difference was used by us to develop a method for removing a microimpurity of cesium from rubidium salts.

It was indicated in the literature (10) that isomorphous relationships exist between RbJ_3 and CsJ_3. To verify this circumstance and to estimate the degree of cocrystallization of cesium with RbJ_3, the cocrystallization coefficients (Khlopin constants) were determined by the method of isothermal removal of supersaturation (20) at variable amounts of the precipitated RbJ_3. The crystallization coefficients (k) were calculated by the formula:

$$k = \frac{x(b-y)}{y(a-x)},$$

where x, y are the amounts of the micro- and macrocomponent (in our case Cs and RbJ_3) in the solid phase, in grams; a, b are the amounts of the micro- and macrocomponent in the liquid phase before crystallization (in grams).

The method for determining these quantities was as follows. In an aliquot portion of a RbJ_3 solution, saturated at temperature T_1, with a known content of the principal component (RbJ_3) and impurity (Cs), an accurately weighed portion of RbJ_3, likewise with a known concentration of cesium impurity,* was dissolved on heating to temperature T_2. From these data it was easy to calculate

the content of the micro- and macrocomponents in the liquid phase before crystallization (a, b). Then the resulting solution was slowly cooled to temperature T_1, after which, for a definite time, the same in all experiments, a mechanical stirrer with a large number of revolutions was turned on. After removal of supersaturation in the mother solution, the cesium content was determined.

The cocrystallization coefficients found for three different amounts of precipitated RbJ_3 proved to be very close to one another (Table 1);

Table 1

Results of determination of Khlopin constants (K) at 25°

Cs content in saturated RbJ_3 solution, % of RbJ_3	Addition of RbJ_3, g	Cs content in the RbJ_3 addition, wt. %	Cs, wt. % of RbJ_3 in mother liquor after crystallization	RbJ_3, g/ml in mother liquor after crystallization	K
0.418	0.4009	2.84	0.327	1.968	23.7
0.418	0.2091	2.84	0.355	1.968	24.4
0.418	0.1505	2.84	0.350	1.968	22

Thus, in the present case the magnitude of the crystallization coefficient does not depend on the amount of the precipitated macrocomponent. This serves as confirmation of the presence of isomorphism between RbJ_3 and CsJ_3.

* The cesium microimpurity was determined in all cases by the method of flame photometry.

A study of the distribution of cesium impurity between the crystalline phase and the solution during crystallization of RbJ_3 thus showed that this process proceeds with concentration of cesium in the precipitate and depletion of cesium in the mother liquor (the mean value of K is 23.3). This provided grounds for concluding that it is possible to remove microimpurities of cesium from an RbJ solution by precipitating cesium during the partial separation of rubidium in the form of RbJ_3. The latter, consequently, should play the role of a carrier for removing microquantities of cesium from the solution.

To determine the optimal conditions for separating RbJ_3 into the precipitate (concentrations of the components in solution, temperature regime), the solubility diagram in the system RbJ—J_2—H_2O, studied in detail ([19]) over a wide temperature range, was used. It follows from it that crystallization should be carried out in the interval from 0 to 5°, at component concentrations in the solution determined by the segment of the RbJ_3 crystallization branch adjacent to the eutonic point RbJ + RbJ_3. As a result of a series of experiments, the

influence on the degree of purification of an RbJ solution from cesium was established for the amount of RbJ_3 separated, the initial content of cesium impurity, the number of precipitations, and the intensity of stirring during crystallization, which has a favorable effect on the purification of the solution from cesium impurity.

It was established that the greatest purification factor (10-20) in a single precipitation is attained at a high initial content of cesium impurity (in our experiments, up to 5%); at a lower initial cesium content ($< 0.1\%$) the purification factor decreases. At the same time, the purification factor depends little on the amount of RbJ_3 separated into the precipitate. Therefore, by successive precipitation from the same solution of small portions, rather than by a single precipitation of a considerable amount of RbJ_3, better results can be achieved (Table 2).

Table 2

Dependence of the degree of purification on the number of fractionation stages

Cs content in the initial RbJ, %	Cs content in solution after a single precipitation of RbJ_3, % of RbJ	Cs content in solution after four precipitations, % of RbJ
0.25	0.02*	0.01**
1.5	0.1*	0.02**

* 50% of the RbJ contained in the solution was separated.
** A total of 40% of the RbJ contained in the solution was separated.

The essence of the method recommended for purifying rubidium salts from microimpurities of cesium by precipitation of isotripolyhalides is as follows. Finely ground crystalline iodine is dissolved in an aqueous RbJ solution heated to 60-80°, calculated so as to separate $\sim$ 10% of the dissolved RbJ (weight ratio $RbJ : H_2O : J_2 = 5 : 5 : 1$) in the form of the first fraction of RbJ_3 contaminated with cesium. The mixture is stirred until the iodine is completely dissolved. Crystallization of RbJ_3 from the resulting solution is carried out with vigorous stirring and cooling with ice to +5°. After this, the precipitated crystals are filtered off, and precipitation of a second fraction of RbJ_3 is carried out under the same temperature conditions, calculated to separate from the solution the same amount of RbJ. In total, n precipitations of RbJ_3 are carried out from the mother liquor (usually 3-4 times, depending on the initial cesium content), giving altogether $(n + 1)$ fractions of contaminated RbJ_3. The final mother liquor is evaporated at 120-130° to dryness, and the dry residue is calcined first at 150° to remove the bulk of the iodine, and then at 300-350° for its complete removal.

The rubidium iodide obtained after calcination contains 0.01% cesium, when its initial content in RbJ was from 0.25 to 2.5%. The yield of purified rubidium in the direct cycle is 55%; the remaining 45% of RbJ is contained in the cesium-enriched precipitate separated during the $(n+1)$-fold precipitation of RbJ_3 in the purification process. The precipitate of contaminated RbJ_3 after preliminary-

the subsequent calcination to RbI is returned to the main part of the purification process scheme, which reduces losses of RbI to a minimum. The iodine removed during calcination can be captured by one of the known methods.

Of course, other rubidium salts besides the iodide can also be purified after converting them to RbI, for example through the tetraoxalate [21] and the carbonate.

Thus, as is evident from the present communication and our preceding work [5], polyhalides of alkali elements that are similar in their properties can be successfully used to obtain rubidium and cesium compounds of high purity.

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Note: Figure translations are in progress. See original paper for figures.