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Study of the Interaction of Antimony(III) Chlorides and Bromides with Alkali Elements Similar in Properties in Solutions of the Corresponding Hydrohalic Acids

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Complex halides of antimony(III) and of alkali elements similar in properties have long attracted the attention of researchers in connection with the possibility of using these salts for the separation of rubidium and cesium from solutions and for the quantitative determination of the latter element.

The first works appeared as early as the 1930s of the last century ([1]), and subsequently many authors devoted attention to the study of this class of compounds. A large number of complex halides of potassium, rubidium, and cesium with the corresponding antimony(III) halides were synthesized both in the process of crystallization from the melt and, predominantly, by isolation from solution. In the literature ([2]) there are reports of the existence of the following double chlorides of potassium and antimony, obtained from solutions: $3KCl \cdot SbCl_3$, $2KCl \cdot SbCl_3$, $23KCl \cdot 10SbCl_3$ (or $7KCl \cdot 3SbCl_3$), some of which were isolated in the form of crystalline hydrates. The double chlorides of rubidium and antimony also, for the most part, differ in the ratio of the components: there is information ([2], [3]) on the compounds $RbCl \cdot 2SbCl_3$, $3RbCl \cdot 2SbCl_3$, $23RbCl \cdot 10SbCl_3$ (or $7RbCl \cdot 3SbCl_3$), $RbCl \cdot SbCl_3$, and on crystalline hydrates of some of them. As for cesium compounds, as a result of a lengthy discussion it was recognized ([3-5]) that there exists a single double chloride—$3CsCl \cdot 2SbCl_3$*. This compound aroused the greatest interest because of its slight solubility, which led researchers to use it for the quantitative determination of cesium ([7]) and for the microdetermination of antimony ([8]). However, these methods did not receive further development. A greater effect was achieved when $3CsCl \cdot 2SbCl_3$ was used for technological purposes—for the separation of cesium from solutions obtained in the decomposition of pollucite by hydrochloric acid ([9]).

Information on the double bromides of alkali elements and antimony is more limited. As in the case of double chlorides, the greater number of works is devoted to compounds of potassium and rubidium. The compositions of the synthesized double bromides are analogous to those of the corresponding double

chlorides ([2], [10]): 2KBr·$SbBr_3$, 3KBr·2$SbBr_3$, 23KBr·10$SbBr_3$ (or 7KBr·3$SbBr_3$), 3RbBr·2$SbBr_3$, 23RbBr·10$SbBr_3$ (or 7RbBr·3$SbBr_3$), 2RbBr·$SbBr_3$. For cesium, only one compound—$3CsBr \cdot 2SbBr_3$—was synthesized ([11]). Like $3CsCl \cdot 2SbCl_3$, it possesses negligible solubility and was recommended ([12]) for precipitating cesium from solutions obtained in the decomposition of pollucite by hydrobromic acid.

Despite the large number of works devoted to double halides of antimony(III) with potassium, rubidium, and cesium, no systematic studies have been carried out, and this can explain the contradictory data on the composition, conditions of formation, and certain properties of the indicated complex compounds. In this connection, and also because of the technological interest** in these

* Only in the work of Moser and Ritschel ([6]) was the question again raised of the possibility of the formation of complex salts of CsCl and $SbCl_3$ of another composition.

** From double halides, owing to their easy hydrolyzability by water and ammonia solutions, it is always easy to pass to simple halides (for example, of cesium), with practically complete regeneration of the precipitant ($SbCl_3$ or $SbBr_3$).

it seemed advisable to study heterogeneous equilibria in quaternary systems formed by $SbCl_3$ and $SbBr_3$ with the corresponding halides of potassium, rubidium, and cesium in solutions of hydrohalic acids.

We investigated the systems MeHal–$SbHal_3$–HHal–H_2O (Me = K, Rb, Cs; Hal = Cl, Br) at a constant concentration of the hydrohalic acids of 5, 10, 15, and, in some cases, 18 and 20 wt. %. Solubility was studied by the isothermal method at 25 ± 0.1°. The controlled equilibrium was established after 20 days. Samples of the liquid phases and "solid residues" were treated with a saturated solution of tartaric acid, which, by binding antimony into a complex, prevented hydrolysis. In the samples the following were determined: antimony by the iodometric method ([13]), the alkali element by the gravimetric method using tetraphenylboron sodium ([14]), and chlorine (or bromine) by the gravimetric method ([13]) as AgCl (or AgBr). Data on the corresponding ternary systems were taken from the literature ([2]) or obtained by us earlier ([15]).

It is known that a four-component system is represented as a regular tetrahedron, the vertices of which correspond to the components of the system; however, in the course of the work we used the central projection onto one of the faces of the tetrahedron: onto the face MeHal–$SbHal_3$–HHal for determining the water content of the compounds formed in the systems, and onto the face MeHal–$SbHal_3$–H_2O for determining the composition of the solid phases and plotting solubility curves, which are the lines of intersection of the crystallization surface in the quaternary system with cutting planes drawn at the level of definite acid concentrations.

Table 1

Main solubility data in the systems KHal–$SbHal_3$–HHal–H_2O at 25°

HCl	HBr	KCl	KBr	$SbCl_3$	$SbBr_3$	Solid phase
5.00	–	20.20	–	–	–	KCl
5.13	–	17.09	–	38.50	–	KCl + A
4.87	–	10.46	–	62.28	–	A + B
4.91	–	3.80	–	78.40	–	B + SbCl
5.00	–	–	–	85.60	–	$SbCl_3$
10.00	–	13.71	–	–	–	KCl
9.91	–	12.00	–	36.04	–	KCl + A
10.11	–	8.56	–	56.69	–	A + B
9.75	–	2.70	–	73.65	–	B + $SbCl_3$
10.00	–	–	–	80.09	–	$SbCl_3$
15.00	–	7.64	–	–	–	KCl
14.80	–	6.37	–	33.18	–	KCl + A
14.70	–	4.25	–	52.17	–	A + B
14.68	–	2.12	–	66.49	–	B
–	5.00	–	34.00	–	–	KBr
–	5.71	–	29.21	–	38.22	onset of hydrolysis
–	10.00	–	27.50	–	–	KBr
–	9.84	–	22.71	–	37.30	KBr + C
–	10.27	–	14.82	–	48.15	onset of hydrolysis
–	15.00	–	21.32	–	–	KBr
–	14.96	–	17.01	–	36.27	KBr + C
–	15.35	–	10.59	–	51.85	C + D
–	14.81	–	5.99	–	62.45	D
–	20.00	–	16.00	–	–	KBr
–	20.07	–	12.01	–	35.45	KBr + C
–	20.25	–	7.09	–	50.78	C + D
–	19.28	–	4.05	–	56.03	D

Note: A –$2KCl \cdot SbCl_3$; B –$3KCl \cdot 2SbCl_3$; C –$2KBr \cdot SbBr_3$; D –$3KBr \cdot 2SbBr_3$.

Table 2

Basic solubility data in the systems RbHal–$SbHal_3$–HHal–H_2O at 25°

HCl	HBr	RbCl	RbBr	$SbCl_3$	$SbBr_3$	Solid phase
5.00	–	35.80	–	–	–	RbCl
4.96	–	35.56	–	1.90	–	RbCl + A
5.07	–	9.94	–	24.83	–	A + B
5.21	–	7.13	–	54.45	–	Beginning of hydrolysis
10.00	–	26.28	–	–	–	RbCl
9.97	–	25.66	–	1.79	–	RbCl + A
9.63	–	8.61	–	25.20	–	A + B
10.20	–	5.29	–	52.60	–	B + C

HCl	HBr	RbCl	RbBr	$SbCl_3$	$SbBr_3$	Solid phase
9.10	–	4.47	–	64.83	–	C
15.00	–	22.61	–	–	–	RbCl
15.04	–	21.68	–	0.48	–	RbCl + A
15.09	–	5.10	–	25.09	–	A + B
15.49	–	4.23	–	51.00	–	B + C
14.82	–	3.82	–	54.43	–	C
–	5.00	–	45.50	–	–	RbBr
–	4.94	–	42.28	–	2.85	RbBr +
–	5.60	–	21.77	–	5.54	Beginning of hydrolysis
–	10.00	–	38.30	–	–	RbBr
–	9.90	–	33.29	–	2.70	RbBr +
–	9.09	–	17.70	–	5.01	+
–	10.05	–	7.65	–	9.89	Beginning of hydrolysis
–	15.00	–	36.35	–	–	RbBr
–	14.91	–	28.96	–	2.39	RbBr +
–	14.94	–	15.47	–	3.83	+
–	15.30	–	2.89	–	25.99	Beginning of hydrolysis
–	20.00	–	24.80	–	–	RbBr
–	20.09	–	23.17	–	1.60	RbBr +
–	20.14	–	11.23	–	3.59	+
–	19.62	–	1.60	–	56.95	

Note. A –$7RbCl \cdot 3SbCl_3$; B –$3RbCl \cdot 2SbCl_3$; C –$RbCl \cdot SbCl_3 \cdot H_2O$; – $2RbBr \times SbBr_3$; –$3RbBr \cdot 2SbBr_3$.

Table 3

Basic solubility data in the systems CsHal–$SbHal_3$–HHal–H_2O at 25°

HCl	HBr	CsCl	CsBr	$SbCl_3$	$SbBr_3$	Solid phase
5.00	–	56.25	–	–	–	CsCl
5.35	–	55.67	–	0.08	–	CsCl + A
5.88	–	47.61	–	0.05	–	A + B
5.23	–	41.20	–	0.038	–	B + C
5.76	–	0.25	–	11.49	–	Beginning of hydrolysis
10.00	–	50.00	–	–	–	CsCl
9.90	–	49.54	–	0.10	–	CsCl + A
9.71	–	42.39	–	0.09	–	A + B
9.89	–	33.20	–	0.048	–	B + C
10.94	–	0.49	–	61.02	–	C
15.00	–	46.95	–	–	–	CsCl
14.08	–	46.73	–	0.068	–	CsCl + A
15.94	–	41.38	–	0.08	–	A + B

HCl	HBr	CsCl	CsBr	$SbCl_3$	$SbBr_3$	Solid phase
14.64	–	27.55	–	0.038	–	B + C
15.82	–	0.44	–	46.92	–	C
18.00	–	44.00	–	–	–	CsCl
18.00	–	43.89	–	0.045	–	CsCl + B
18.10	–	25.05	–	0.06	–	B + C
17.94	–	0.18	–	42.30	–	C
–	5.00	–	47.50	–	–	CsBr
–	5.61	–	45.93	–	0.038	CsBr +
–	5.50	–	–	–	2.10	Beginning of hydrolysis
–	10.00	–	40.50	–	–	CsBr
–	9.83	–	39.84	–	0.035	CsBr +
–	9.80	–	–	–	13.60	Beginning of hydrolysis
–	15.00	–	34.00	–	–	CsBr
–	15.14	–	32.72	–	0.045	CsBr +
–	14.71	–	–	–	36.20	Beginning of hydrolysis
–	20.00	–	27.75	–	–	CsBr
–	21.07	–	26.76	–	0.037	CsBr +
–	18.97	–	–	–	64.09	

Note. A –$4CsCl \cdot SbCl_3$; B –$5CsCl \cdot 2SbCl_3$; C –$3CsCl \cdot 2SbCl_3$; –$3CsBr \cdot 2SbBr_3$.

The results of the study of the systems are given, for brevity, in Tables 1-3 in the form of the coordinates of the nodal and last investigated points of the solubility curves, as well as the corresponding solid phases. The appearance of these last points on the solubility curves is explained by the onset of hydrolysis or by the impossibility of attaining the required concentration of hydrogen halide in the system at high contents of $SbCl_3$ or $SbBr_3$.

Thus, as a result of the study of the systems MeHal–$SbHal_3$–HHal–H_2O, the number of phases crystallizing in them, their composition, and the conditions and limits of their existence have been unambiguously established.

All the double salts found in the systems studied, the properties of which are given in Table 4, were identified by X-ray phase analysis.

Table 4

Some properties of double chlorides and bromides of potassium, rubidium, cesium, and antimony(III)

Compound	Optical characteristics of the crystals	Density at 25°, g/cm^3	Note
$2KCl \cdot SbCl_3$	Anisotropic, biaxial; $N_g = 1.773$; $N_p = 1.745$	2.61	i.s.
$3KCl \cdot 2SbCl_3$	Anisotropic, biaxial; $N_g = 1.774$; $N_p = 1.761$	2.57	i.s., i.m. at 291°
$7RbCl \cdot 3SbCl_3$	Anisotropic, biaxial, positive; $N_g = 1.754$; $N_m = 1.739$; $N_p = 1.734$	2.93	c.s.
$3RbCl \cdot 2SbCl_3$	High birefringence, oblique extinction; $n > 1.780$	3.16	i.s.
$RbCl \cdot SbCl_3 \cdot H_2O$	Anisotropic, oblique extinction; $N_g > 1.780$; $N_p = 1.767$	3.16	i.s.
$4CsCl \cdot SbCl_3$	Anisotropic; $N_g = 1.712$; $N_p = 1.704$	3.37	i.s.
$5CsCl \cdot 2SbCl_3$	Anisotropic; $n > 1.780$	3.55	i.s.
$3CsCl \cdot 2SbCl_3$	Anisotropic; $n > 1.780$	3.45	c.s., c.m. at 540°
$2KBr \cdot SbBr_3$	High birefringence, oblique extinction; $n > 1.780$	3.55	i.s.
$3KBr \cdot 2SbBr_3$	Anisotropic; $n > 1.780$	3.68	i.s., i.m. at 300°
$2RbBr \cdot SbBr_3$	Anisotropic; $n > 1.780$	3.86	c.s.

Compound	Optical characteristics of the crystals	Density at 25°, g/cm^3	Note
$3RbBr \cdot 2SbBr_3$	Anisotropic; $n > 1.780$	3.68	i.s.
$3CsBr \cdot 2SbBr_3$	Anisotropic; low birefringence; $n > 1.780$	4.23	c.s., c.m. at 625°

Note. i.s.—dissolves incongruently; i.m.—melts incongruently; c.s.—dissolves congruently; c.m.—melts congruently (data on the nature of melting are taken from our work [16], devoted to the study of the fusibility of the MeHal–$SbHal_3$ systems).

The clear difference in the solubility of compounds formed in systems containing $SbCl_3$ and KCl or RbCl indicates the possibility of separating potassium and rubidium, which are similar in their properties. The solubility data for systems containing cesium indicate the possibility of carrying out the precipitation of cesium in the form of $3CsCl \cdot 2SbCl_3$ or $3CsBr \cdot 2SbBr_3$ under optimum conditions, with a considerable reduction in the acidity of the medium.

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