Solvent Extraction of Antimony(V) as Hexachloroantimonate(V) with Quaternary Ammonium Ions

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The extraction of antimony from an aqueous halide medium into an organic solvent has been frequently used for both the separation and spectrophotometric determination of antimony. The methods for the solvent extraction-photometric determination of antimony(V) based on the extraction of the ion-association complexes of the chloride-complex (SbCl_6^-) of antimony(V) with cations of some dyes, such as Malachite Green,¹ Brilliant Green,¹⁻⁴ Crystal Violet,^{1,2,5} Ethyl Violet² and Rhodamine B⁶⁻¹² have been reported. However, the equilibrium for the solvent extraction of the ion associates of hexachloroantimonate(V) has not been studied.

In the present work, the extraction constants ($\log K_{\text{ex}}$) for the ion associates of hexachloroantimonate(V) ion with various quaternary ammonium ions distributed between an aqueous and four organic phases (chloroform, benzene, toluene and carbon tetrachloride) were determined and correlated with the number of carbon atoms in the quaternary ammonium ions. The extractability of hexachloroantimonate(V) was also considered based on those of other metal-halogeno complex anions.¹³⁻¹⁸

Experimental

Apparatus

The apparatus for recording spectra and absorbance measurements, horizontal shaking and phase separation after extraction were described in a previous paper.¹⁹

Reagents

The supplier and purity of quaternary ammonium ions, and the preparation of the quaternary ammonium ion solutions were as described in a previous paper.¹⁵ A standard antimony(III) solution (4×10^{-4} M) was prepared by dissolving antimony(III) chloride with 8 M hydrochloric acid solution. Hydrochloric acid was used for the formation of a antimony(V)-chloro complex. Cerium(IV) sulfate solution was prepared by dissolving with a diluted sulfuric acid solution, and was employed as the oxidant for the oxidation of Sb(III) to Sb(V). A hydroxylammonium chloride aqueous solution was employed as the reductant for the reduction of any excess cerium(IV) sulfate. Commercially available chloroform, benzene, toluene and carbon tetrachloride were used without further purification, and were saturated with distilled water before use.

Standard procedure for a stoichiometry measurement

One milliliter of a 4×10^{-4} M antimony(III) solution was

transferred to a 25 ml stoppered test-tube; then, 0.5 ml of a 9.44 M hydrochloric acid solution, 0.5 ml of a 2×10^{-2} M cerium (IV) sulfate solution (in 6 M sulfuric acid), 1 ml of a 15 M sulfuric acid solution, 2 ml of concentrated hydrochloric acid solution, 0.5 ml of a 0.2 M hydroxylammonium solution and an appropriate amount of aqueous quaternary ammonium salt solution were added. The solution was diluted to 6 ml with distilled water. The aqueous solution was mechanically shaken with 6 ml of an extracting solvent for 20 min at 25°C. After centrifugation of the mixture, the absorbance at 280 nm of the aqueous phase was measured for the determination of antimony.

Calculation of the extraction constants

In the chloride-ion concentration of 6 M, the antimony(V)-chloro complex, SbCl_6^- , is mainly formed.^{20,21} Hexachloroantimonate(V) anion, SbCl_6^- distributes between the aqueous and organic phases:

and

$$K_{\text{ex}(\text{SbCl}_6^-)} = [\text{Q}^+ \cdot \text{SbCl}_6^-]_{\text{org}} / [\text{Q}^+][\text{SbCl}_6^-], \quad (2)$$

where K_{ex} is the extraction constant; the subscript "org" refers to the organic phase and the absence of a subscript indicates the aqueous phase. The distribution ratio of antimony between the aqueous and organic phases (D_{Sb}) is given by

$$D_{\text{Sb}} = \frac{[\text{Q}^+ \cdot \text{SbCl}_6^-]_{\text{org}}}{[\text{SbCl}_6^-]}. \quad (3)$$

Hence, the following equation can be derived from Eqs. (2) and (3):

$$D_{\text{Sb}} = K_{\text{ex}(\text{SbCl}_6^-)} \cdot [\text{Q}^+], \quad (4)$$

where

$$\log D_{\text{Sb}} = \log K_{\text{ex}(\text{SbCl}_6^-)} + \log [\text{Q}^+]. \quad (5)$$

The quaternary ammonium ions will form ion associates with a foreign anion, as shown in Eq. (6); these are also extracted into the organic phase:

Fig. 1 Effect of the extracting solvent on the absorption spectra in the aqueous phase. (1) Sb: 6.67×10^{-5} M, HCl: 6 M, H_2SO_4 : 3 M, $\text{Ce}(\text{SO}_4)_2$: 1.67×10^{-3} M, HONH_3Cl : 1.67×10^{-2} M; with extraction: (2) carbon tetrachloride, (3) chloroform, (4) toluene, (5) benzene; reference: distilled water.

Fig. 2 Absorption spectra of antimony(V)-chloro complex in aqueous solution. Sb ($\times 10^{-5}$ M): (1) 1.33, (2) 2.67, (3) 4.00, (4) 5.34, (5) 6.67; HCl: 6 M; H_2SO_4 : 3 M; $\text{Ce}(\text{SO}_4)_2$: 1.67×10^{-3} M; HONH_3Cl : 1.67×10^{-2} M; reference: reagent blank.

$$K_{\text{ex}(\text{X}^-)} = [\text{Q}^+\text{X}^-]_{\text{org}} / [\text{Q}^+][\text{X}^-], \quad (6)$$

where X^- is Cl^- .

The side-reaction coefficient for the quaternary ammonium ion ($\alpha_{\text{Q}^+(\text{X}^-)}$) is given by

$$\begin{aligned} \alpha_{\text{Q}^+(\text{X}^-)} &= \frac{[\text{Q}^+]' }{[\text{Q}^+]} = \frac{[\text{Q}^+] + [\text{Q}^+\text{Cl}^-]_{\text{org}}}{[\text{Q}^+]} \\ &= 1 + K_{\text{ex}(\text{Cl}^-)}[\text{Cl}^-] \end{aligned} \quad (7)$$

where $[\text{Q}^+]'$ is the total concentration of the quaternary ammonium ion that is not bound in ion associates with hexachloroantimonate(V), and $K_{\text{ex}(\text{Cl}^-)}$ is the extraction constants of a quaternary ammonium ion with chloride ion. $[\text{Q}^+]$ can be calculated by

$$[\text{Q}^+] = [\text{Q}^+]' / \alpha_{\text{Q}^+(\text{X}^-)}. \quad (8)$$

Results and Discussion

Examination of the optimal conditions for determining the extraction constants

Antimony(III) is converted with cerium(IV) sulfate to hexachloroantimonate(V) in a hydrochloric acid medium. The maximum absorbance of the hexachloroantimonate(V) ion is at 272 nm,²² and antimony can be determined from the molar absorptivity of the hexachloroantimonate(V). The effect of the concentration of cerium(IV) sulfate on the formation of hexachloroantimonate(V) was examined in 6 M hydrochloric acid. SbCl_6^- formed in a hydrochloric acid medium was extracted into diisopropyl ether as HSbCl_6 to prevent the hydrolysis of SbCl_6^- , and the absorbance of the diisopropyl ether phase was measured at 272 nm. The maximum and constant absorbances were obtained at concentrations of cerium(IV) sulfate above 1.34×10^{-3} M. Therefore, 1.67×10^{-3} M cerium(IV) sulfate was employed in this work.

Cerium(IV) sulfate, used as the oxidant, showed a weak absorption at near 270 nm in an aqueous solution, which affected the absorption of SbCl_6^- in ultraviolet region. Hydroxylammonium chloride was employed as the reductant for the reduction of the excess of cerium(IV) sulfate and 1.67×10^{-2} M hydroxylammonium chloride was adequate for this purpose.

Neumann²² has reported that SbCl_6^- easily undergoes a

hydrolysis reaction in a hydrochloric acid solution of low acidity to form $\text{Sb}(\text{OH})\text{Cl}_5^-$ and higher hydroxy species. Neumann and Ramette²³ have studied the rate of this hydrolysis and, in 6 M hydrochloric acid, have reported it to be about 1% per min at room temperature. Burke *et al.*²⁴ have shown that this rate of hydrolysis can be considerably slowed by the use of mixed hydrochloric acid-sulfuric acid media. The effect of the concentrations of hydrochloric acid and sulfuric acid on the hydrolysis of SbCl_6^- was examined by measuring the absorbance at 272 nm in an aqueous solution. The acidity with 6 M hydrochloric acid and 3 M sulfuric acid was optimum for this experiment. Under these conditions, about 10 min was allowed for the reduction of the excess of cerium(IV) sulfate and the absorbance at 272 nm was kept to be constant within 1 h.

The absorption spectra of the aqueous phases in the ultraviolet region after extraction with carbon tetrachloride, toluene, benzene and chloroform are shown in Fig. 1. With toluene and benzene extraction systems, the large absorption are shown at near 260 nm and 250 nm, respectively, which affect the absorbance measurement at 272 nm for SbCl_6^- . The effect of these extracting solvents can be neglected by measuring the absorbance at 280 nm. The absorption spectra of the hexachloroantimonate(V) in aqueous solution is shown in Fig. 2. A calibration graph obtained for antimony was linear over the 0 – 6.67×10^{-5} M range. The molar absorptivity for antimony was about $6.6 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 280 nm.

Determination of the extraction constants

In the extraction of hexachloroantimonate(V), the distribution ratios of antimony at different concentrations of the quaternary ammonium ions were determined. The values of $\log D_{\text{Sb}}$ were plotted against $\log[\text{Q}^+]$. As expected from Eq. (5), straight lines with slopes almost equal to about one were obtained for almost all of the extraction systems, except for TEA and TPA of the carbon tetrachloride extraction system. However, straight lines with slopes of 1.33 and 1.45 were obtained for TEA and TPA of the carbon tetrachloride extraction system, respectively. The reasons for these results are not clear. This means that the extraction equilibrium shown in Eq. (1) holds, and that the extracted species was $\text{Q}^+\text{SbCl}_6^-$. The extraction constants calculated from Eq. (5) are summarized in Table 1; the standard deviation is very small.

Relationship between the extraction constants and the number of carbon atoms in the quaternary ammonium ion and effect of

Table 1 Extraction constants ($\log K_{\text{ex}}$) obtained between aqueous and organic phases

Extracting solvent	Q^+ cation ^a	$\log K_{\text{ex}}$		Slope of $\log D_{\text{SB}}$ v.s. $\log [Q^+]$ plots
		SbCl_6^{-b}	Cl^{-c}	
Carbon tetrachloride	TEA	2.44 ± 0.07 (3)	-12.26	1.33
	TPA	4.06 ± 0.08 (4)	-9.90	1.45
	TBA	5.33 ± 0.10 (6)	-7.54	0.94
	OTMA	3.53 ± 0.07 (6)	-9.29	1.19
	DTMA	4.08 ± 0.03 (4)	-8.11	1.00
	DDTMA	4.87 ± 0.11 (6)	-6.93	1.03
Toluene	TEA	2.45 ± 0.02 (4)	-11.26	1.08
	TPA	3.78 ± 0.06 (5)	-8.90	0.98
	TBA	4.89 ± 0.09 (9)	-6.54	1.19
	HTMA	2.90 ± 0.07 (11)	-9.47	1.10
	OTMA	3.95 ± 0.03 (3)	-8.29	0.81
	DTMA	5.02 ± 0.06 (6)	-7.11	0.98
Benzene	TEA	2.90 ± 0.01 (3)	-10.46	1.13
	TPA	3.88 ± 0.05 (11)	-8.10	1.03
	TBA	5.43 ± 0.05 (4)	-5.74	0.90
	HTMA	3.45 ± 0.05 (10)	-8.67	1.06
	OTMA	4.46 ± 0.06 (6)	-7.49	1.14
	DTMA	5.32 ± 0.09 (7)	-6.31	1.09
Chloroform	TEA	2.90 ± 0.05 (7)	-4.56	0.90
	TPA	5.18 ± 0.06 (9)	-2.20	0.93
	HTMA	3.70 ± 0.06 (10)	-2.77	1.07
	OTMA	4.98 ± 0.04 (5)	-1.59	0.99

a. TEA, tetraethylammonium chloride; TPA, tetrapropylammonium chloride; TBA, tetrabutylammonium chloride; HTMA, hexyltrimethylammonium bromide; OTMA, octyltrimethylammonium chloride; DTMA, dodecyltrimethylammonium chloride; DDTMA, dodecyltrimethylammonium chloride; TDTMA, tetradecyltrimethylammonium chloride.

b. Mean value $\pm$ standard deviation. The figures in parentheses are the numbers of measurements.

c. Ref. 25.

Fig. 3 Relation between $\log K_{\text{ex}}$ and the number of carbon atoms in the quaternary ammonium ion. (1) alkyltrimethylammonium ions ($\circ$): (a) HTMA, (b) OTMA; (2) tetraalkylammonium ions ($\bullet$): (c) TEA, (d) TPA; extracting solvent: chloroform.

the extracting solvent

The values of the extraction constants ($\log K_{\text{ex}}$) were plotted against the number of carbon atoms in the quaternary ammonium ion (N_c). The results obtained for the chloroform, benzene, toluene and carbon tetrachloride extraction systems are shown in Figs. 3 – 6, respectively. For the same carbon number,

Fig. 4 Relation between $\log K_{\text{ex}}$ and the number of carbon atoms in the quaternary ammonium ion. (1) alkyltrimethylammonium ions ($\circ$): (a) HTMA, (b) OTMA, (c) DTMA; (2) tetraalkylammonium ions ($\bullet$): (d) TEA, (e) TPA, (f) TBA; extracting solvent: benzene.

Fig. 5 Relation between $\log K_{\text{ex}}$ and the number of carbon atoms in the quaternary ammonium ion. (1) alkyltrimethylammonium ions ($\circ$): (a) HTMA, (b) OTMA, (c) DTMA; (2) tetraalkylammonium ions ($\bullet$): (d) TEA, (e) TPA, (f) TBA; extracting solvent: toluene.

the extractability ($\log K_{\text{ex}}$) with long-chain alkyltrimethylammonium cations (group I) is larger than that with symmetrical tetraalkylammonium cations (group II) for chloroform, benzene and toluene extraction systems; the extractability ($\log K_{\text{ex}}$) with group I was almost the same as that with group II for carbon tetrachloride extraction system. The ion association reaction in a low-polar solvent extraction process is based on a hydrophobic interaction and an electrostatic interaction: the effect of the former on the ion association is larger than that of the latter, which contributes to an increase in $\log K_{\text{ex}}$ value with increasing N_c . For chloroform, benzene and toluene extraction systems, the differences in the $\log K_{\text{ex}}$ values between these two group I and group II cations for the same carbon number indicates that the electrostatic attraction of the cations in group I for the anionic complex is larger than that of the cations in group II, which can be explained by an effect of the flexibility

Table 2 Contribution of a methylene group to extraction constant ($\log K_{\text{ex}}$)

Extracting solvent ^a	Anion	$\Delta \log K_{\text{ex}}/\text{CH}_2$	
		Alkyltrimethylammonium cation	Tetraalkylammonium cation
CF	CuCl ₂ ⁻	0.61(ref.13)	0.58(ref.13)
	GaCl ₄ ⁻	0.69(ref.14)	0.75(ref.14)
	TiCl ₄ ⁻	0.59(ref.15)	0.62(ref.15)
	AuCl ₄ ⁻	0.53(ref.16)	0.54(ref.16)
	SbCl ₆ ⁻	0.64	0.57
	InBr ₄ ⁻	0.90(ref.17)	0.85(ref.17)
	AuBr ₄ ⁻	0.82(ref.16)	0.51(ref.16)
	TlBr ₄ ⁻	0.47(ref.15)	0.73(ref.15)
	BiI ₄ ⁻	0.54(ref.18)	0.40(ref.18)
	TlI ₄ ⁻		0.28(ref.15)
	PdCl ₄ ²⁻	0.59(ref.26)	0.56(ref.26)
	PtCl ₆ ²⁻	0.59(ref.27)	0.67(ref.27)
	PdBr ₄ ²⁻	0.63(ref.26)	0.67(ref.26)
	PdI ₄ ²⁻	0.60(ref.26)	
	Mean±standard deviation	0.63±0.12	0.59±0.15
B	GaCl ₄ ⁻	0.54(ref.14)	0.45(ref.14)
	TiCl ₄ ⁻	0.41(ref.15)	0.41(ref.15)
	AuCl ₄ ⁻	0.69(ref.16)	0.39(ref.16)
	SbCl ₆ ⁻	0.47	0.32
	InBr ₄ ⁻	0.48(ref.17)	0.40(ref.17)
	AuBr ₄ ⁻	0.67(ref.16)	0.36(ref.16)
	TlBr ₄ ⁻	0.68(ref.15)	0.39(ref.15)
	TlI ₄ ⁻		0.61(ref.15)
	Mean±standard deviation	0.56±0.12	0.42±0.09
T	GaCl ₄ ⁻	0.55(ref.14)	0.49(ref.14)
	AuCl ₄ ⁻	0.58(ref.16)	0.41(ref.16)
	SbCl ₆ ⁻	0.54	0.31
	InBr ₄ ⁻	0.50(ref.17)	0.41(ref.17)
	AuBr ₄ ⁻	0.59(ref.16)	0.35(ref.16)
	Mean±standard deviation	0.55±0.04	0.39±0.07
CTC	GaCl ₄ ⁻	0.59(ref.14)	0.45(ref.14)
	AuCl ₄ ⁻	0.54(ref.16)	0.46(ref.16)
	SbCl ₆ ⁻	0.33	0.37
	AuBr ₄ ⁻	0.40(ref.16)	0.31(ref.16)
	PtCl ₆ ²⁻	0.57(ref.27)	
	Mean±standard deviation	0.49±0.11	0.40±0.07

a. Solvent: CF, chloroform; B, benzene; T, toluene; CTC; carbon tetrachloride.

of a quaternary ammonium ion: the flexibility of the alkyltrimethylammonium ion decreases the distance between the cation and the anion. From the slope of the line in Figs. 3 – 6, the contribution of a methylene group in the cations of group I and II to $\log K_{\text{ex}}$ ($\Delta \log K_{\text{ex}}/\text{CH}_2$) was found to be 0.64 and 0.57, 0.47 and 0.32, 0.54 and 0.31, and 0.33 and 0.37 for chloroform, benzene, toluene and carbon tetrachloride extraction systems, respectively. The values of $\Delta \log K_{\text{ex}}/\text{CH}_2$ for the chloroform extraction system are larger than those for the other three extraction systems. This may be caused by an effect of the solvation of chloroform on the ion associates of hexachloroantimonate(V) with the quaternary ammonium ions: the ion associates are more solvated by chloroform than by the other extracting solvents, and the ion associates are more easily extracted into chloroform. The values of $\Delta \log K_{\text{ex}}/\text{CH}_2$ for hexachloroantimonate(V) are varied by the type of the quaternary ammonium cations and extracting solvents. The values of $\Delta \log K_{\text{ex}}/\text{CH}_2$ for various metal-halogeno complex anions are listed in Table 2. The values of $\Delta \log K_{\text{ex}}/\text{CH}_2$ for hexachloroantimonate(V) are in good agreement with the previously reported values.^{13-19,26-32}

Fig. 6 Relation between $\log K_{\text{ex}}$ and the number of carbon atoms in the quaternary ammonium ion. (1) alkyltrimethylammonium ions (○); (a) OTMA, (b) DTMA, (c) DDTMA; (2) tetraalkylammonium ions (●): (d) TEA, (e) TPA, (f) TBA; extracting solvent: carbon tetrachloride.

Table 3 Extraction constants of ion associates of various metal-halogeno complex anions with octyltrimethylammonium cation in chloroform-extraction

X ⁻	Metal-halogeno complex	$\log K_{\text{ex}}$	$\Delta \log K_{\text{ex}}$
Cl ⁻	CuCl ₂ ⁻	1.57 (ref.13)	
	GaCl ₄ ⁻	3.22 (ref.14)	1.65
	TiCl ₄ ⁻	3.66 (ref.15)	0.44
	AuCl ₄ ⁻	4.23 (ref.16)	0.57
	SbCl ₆ ⁻	4.98	0.75
Br ⁻	InBr ₄ ⁻	2.31 (ref.17)	
	AuBr ₄ ⁻	4.97 (ref.16)	2.66
	TlBr ₄ ⁻	5.33 (ref.15)	0.36
I ⁻	BiI ₄ ⁻	5.31 (ref.18)	

Among the ion associates examined, the extractability values of the extracting solvent were in the order chloroform > benzene > toluene > carbon tetrachloride, which agrees with the order of the value of the transition energy as a parameter of polarity of the extracting solvent; the difference in the $\log K_{\text{ex}}$ between two successive solvents in this order was about 0.52, 0.41 and 0.13 on the average.

Extractability of hexachloroantimonate(V)

The extraction constants ($\log K_{\text{ex}}$) for the 1:1 ion associates of metal-halogeno complex anions with OTMA⁺ into the chloroform extraction are listed in Table 3. From these values, it was found that the extractability of metal-halogeno complex anions was in the order TlBr₄⁻ > BiI₄⁻ > SbCl₆⁻ > AuBr₄⁻ > AuCl₄⁻ > TiCl₄⁻ > GaCl₄⁻ > InBr₄⁻ > CuCl₂⁻; the differences in $\log K_{\text{ex}}$ between two halogeno complex anions in this order were 0.02, 0.33, 0.01, 0.74, 0.57, 0.44, 0.91 and 0.74. This indicates

that, in general, the larger is the coordination number, and the size of the ligand (halide ion: $I^- (2.20 \text{ \AA}) > Br^- (1.96 \text{ \AA}) > Cl^- (1.81 \text{ \AA})^{33}$) and metal ions ($Cu^+ (0.96 \text{ \AA}) > Tl^{3+} (0.95 \text{ \AA}) > In^{3+} (0.81 \text{ \AA}) > Ga^{3+} (0.62 \text{ \AA})^{33}$) for monovalent metal-halogeno complex anions, the greater is the ion associability. The extractability of $SbCl_6^-$ is about 2570 times that of $CuCl_2^-$ with respect to the monovalent chloro complex anion.

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