Separation of natural trivalent oxides of arsenic and antimony

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ABSTRACT

It is demonstrated that arsenic oxide can be extracted from materials containing also antimony oxide using a mixed solvent of 1-butanol and n-heptane. The condition is that water generated as a result of esterification is completely removed from the reaction zone as an azeotrope. The ternary liquid system water + n-heptane + 1-butanol forms three binary azeotropes and a ternary saddle azeotrope. Hydrolysis of tributyl arsenite gives As_2O_3 with a 90–92% yield. The yield of Sb_2O_3 is almost 100%. The organic heptane + butanol mixture can be used for re-extraction of arsenic (III) from a new portion of the mixture of oxides. Thus, the process is cyclic and economically viable; it does not involve high temperature metal roasting harmful for the environment; energy costs of the process are much lower than those of roasting.

1. Introduction

As chalcophiles, arsenic and antimony are found in nature mainly as sulfides and other compounds of sulfur [1–3]. However, they are also found as oxoforms—especially antimony—and frequently together as elementary analogs. Thus, for example Algerian natural senarmontite (antimony ore) contains up to 7% arsenic oxide (As_2O_3), with the content of 20–30% antimony oxide (Sb_2O_3) [4]. Similarly, copper ores desired for their copper are increasingly found to contain higher levels of arsenic and antimony contaminants. While copper smelters are now not emitting arsenic in such amounts as in the past [5], there are problems with arsenic accumulation resulting from human activities for past 100 years or so.

From ores that contain high content of arsenic and antimony (12% or more), those elements are generally extracted by means of oxidizing roasting. Arsenic is usually sublimated between 300 and 600 °C as "white arsenic" (arsenic oxide) [2] while for the purpose of full transition of antimony to an oxoform (Sb_2O_3) the material is subjected to an additional roasting above 800 °C [3]. However, the pyrometallurgical method of separation alone has failed to ensure the obtaining of prime high-purity products. In their work on selective leaching of As and Sb contained in anode slimes, Fernández et al. [4] report that although pyrometallurgical and hydrometallurgical processes "dissolve most of the elements present in anode slimes, treatment of the leaching solutions becomes complex, since the separation of the multiple components is difficult". Notwithstanding the well-developed laboratory methods of separation of these elements [2,3], such methods still have not found a large-scale application under plant conditions due to a number of technical problems. Moreover and evidently, roasting at the temperatures indicated involves high-energy costs.

The purpose of this work was to develop a new and effective method of separation of arsenic (III) and antimony (III) oxides—applicable also on a large scale and *without* high temperature metal roasting that is costly as well as harmful to the environment.

2. Experimental

Seven experiments have been conducted in the same manner, with the amounts of starting compounds and the yields of prime products presented in Table 1. The procedure is described as follows (with amounts corresponding to Experiment 1). In the Dean-Stark apparatus and a return condenser provided with a calcium chloride tube, a suspension consisting of 87.5 g (0.3 mole) antimony oxide (III), 19.8 g (0.10 mole) arsenic oxide (III), 53.4 g (0.720 mole) n-butyl alcohol, and 35 ml n-heptane was boiled until complete

Table 1
Quantities of starting compounds and yields of main products.

Quantities of starting compounds										Yields of main products					
Sb_2O_3		As_2O_3		C_4H_9OH				Heptane (ml)	$C_4H_9OH:C_7H_{16}$ (vol.)	Sb_2O_3			As_2O_3		
g	mole	g	mole	R	g	ml	mole			g	mole	%	g	mole	%
87.5	0.3	19.8	0.1	$n\text{-}C_4H_9$	53.37	66	0.72	35	02:01.1	87.27	0.3	100	17.8	0.09	90
58.3	0.2	39.6	0.2	$n\text{-}C_4H_9$	106.7	132	1,440	60	02:01.1	58	0.2	100	36.1	0.18	91
29.2	0.1	59.3	0.3	$n\text{-}C_4H_9$	160.1	198	2.16	105	02:01.1	29.07	0.1	100	54.8	0.28	92
29.2	0.1	79.1	0.4	$n\text{-}C_4H_9$	213.5	264	2.88	140	02:01.1	29	0.1	100	73.9	0.37	93
117	0.4	19.8	0.1	$iso\text{-}C_4H_9$	53.37	67	0.72	35	02:01.0	115.4	0.4	99	17.9	0.09	91
87.5	0.3	39.6	0.2	$iso\text{-}C_4H_9$	106.7	133	1.44	70	02:01.0	87.1	0.3	100	36	0.18	91
58.3	0.2	59.3	0.3	$iso\text{-}C_4H_9$	160.1	200	2.16	105	02:01.1	57.89	199	99	55.1	0.28	93

water separation (4 h). At the end 5.5 g water was separated. After cooling, the alcohol + heptane phase was accurately separated by decantation and filtered, the sediment treated with 50 ml heptane and dried in a vacuum desiccator over phosphorus pentoxide and paraffin until a fixed mass was formed. 87.3 g (0.299 moles) antimony oxide (III) was produced from the sediment, constituting 99.8% of the theoretical value. Found: 83.67% Sb_2O_3; calculated 83.53% Sb_2O_3.

For the purpose of regenerating As_2O_3, the alcohol + heptane filtrate was treated with 20 ml of double distilled water. The precipitate was washed with water and ethyl alcohol and dried to the constant mass. A crystallized substance of 17.80 g (0.020 moles) of arsenic oxide was obtained, what is 90.0% of the theoretically expected value. Found: 75.31% As_2O_3, calculated 75.74% As_2O_3. The volume of the separated mixture of butyl alcohol and heptane was 94.4 ml, that is 93.5% of the starting amount.

3. Results and discussion

It was reported long ago [6] that arsenic oxide can be extracted from mixtures containing compounds of other metals by higher monohydric alcohols of the aliphatic series:

$$As_2O_3 + 6ROH \rightleftharpoons 2(RO)_3As + 3H_2O \qquad (1)$$
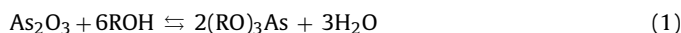
where R is amyl or longer.

Based on this reaction, we attempted to separate arsenic (III) and antimony (III) oxides using amyl and higher alcohols. Our attempts, however, were unsuccessful; antimony oxide was also extracted. Therefore, we have decided to use lower alcohols instead.

We have found that butyl alcohols are suitable for the purpose. We have used mixtures of arsenic and antimony oxides. It has been demonstrated long ago by one of us [7] that as a result of reaction of alcohols with arsenic oxide, tri-n-butyl arsenite is obtained. For n-butanol the reaction proceeds as follows:

$$6n\text{-}C_4H_9OH + As_2O_3 \rightleftharpoons 2(n\text{-}C_4H_9O)_3As + 3H_2O \qquad (2)$$
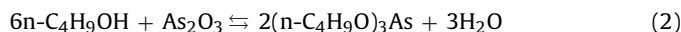
We find that n-butanol reacts *only* with As(III) oxide forming tri-n-butyl arsenite—with 27% yield; Sb_2O_3 remains as a sediment. The sediment was investigated by infrared spectroscopy and the presence of As in it not detected.

The resulting water is removed by distillation of the mixture since a binary azeotrope water + n-butanol exists [8,9]. It boils at 92.3 °C under atmospheric pressure and contains the mole fraction of water $y_{water} = 0.754$ [9]. Thus, with the excess of butanol in the system, water can be removed. Pure n-butanol under 1 atm pressure boils at 117.6 °C [9]. The outcome is a *positive* azeotrope, with the vapor pressure P as a function of composition at a constant temperature T exhibiting positive deviations from the Raoult law and a maximum at the azeotropic point. Necessarily, the diagram of boiling temperature T_b as a function of composition for 1 atm has a minimum at the azeotropic point.

For that matter t-butanol is also in use for water removal [10]. A theory of binary and ternary azeotrope formation in terms of intermolecular interactions has been developed already in the 1960s by Malesinski [11].

As noted, reaction (2) has a low yield of tri-n-butyl arsenite. The problem is the reaction reversibility since n-butanol is partly soluble in water, 9 g/100 ml. Therefore, we have decided to explore also a modification of our azeotrope formation method for water entrainment.

In particular, we have investigated addition of n-heptane for more effective water removal from the reaction medium:

$$6\,n\text{-}C_4H_9OH + As_2O_3 \xrightarrow{n\text{-}C_7H_{16}} 2(n\text{-}C_4H_9O)_3As + 3H_2O \qquad (3)$$
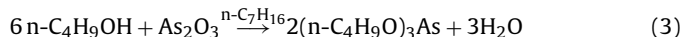
The difference between reactions (2) and (3) is that in reaction (3) the reversibility is practically removed.

Information on the water + n-heptane and n-butanol + n-heptane azeotropes is available [9]. At atmospheric pressure the 1-butanol + n-heptane azeotrope boils at $T_b = 93.4$ °C and contains $y_{1\text{-butanol}} = 0.227$. Also at 1 atm for the water + n-heptane azeotrope the parameters are $T_b = 79.2$ °C and $y_{water} = 0.451$. The normal boiling point of n-heptane is $T_b = 98.4$ °C [9]. With three binary positive azeotropes, there is also a ternary azeotrope. Its parameters are: $y_{water} = 0.24$, $y_{1\text{-butanol}} = 0.50$, $y_{n\text{-heptane}} = 0.26$, $T_b = 90.5$ °C. Note that this is a saddle (positive–negative) azeotrope since its normal boiling point is between the boiling points of the three binary azeotropes.

Since azeotrope formation is the basis of our separation method, we present in Fig. 1 the Gibbs triangle for the ternary liquid system at 1 atm pressure: water + n-heptane + 1-butanol. All four
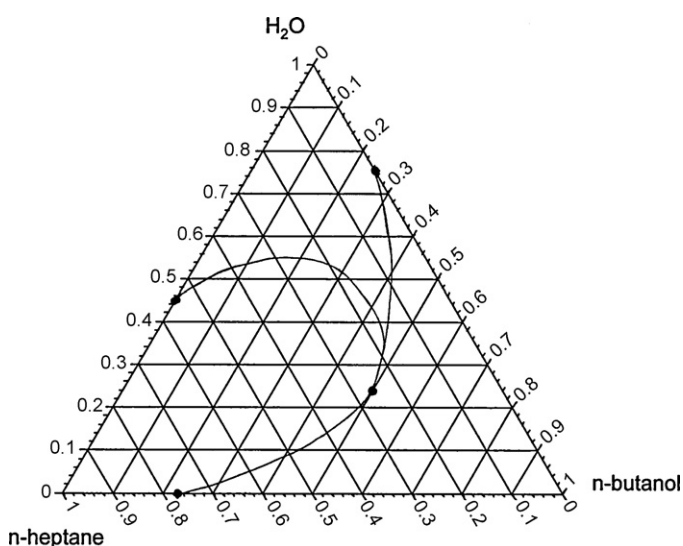

Fig. 1. Binary and ternary azeotropes and approximate valley lines on the normal boiling temperature surface in the system water + n-heptane + 1-butanol.

azeotropes are displayed in Fig. 1 which represents a 2-dimensional projection on the Gibbs triangle from the 3-dimensional surface of normal boiling temperatures above the triangle. We thus see approximate valley lines of boiling temperatures at the normal pressure vs. composition. As their name shows, the valley lines connect minima of boiling temperatures; in polyazeotropic systems they connect the azeotropic points. For any ternary composition of a liquid ternary system, the diagram provides information on the starting composition of the vapor phase formed in a one-stage distillation process.

Given the composition of the ternary azeotrope, per 1 mole of arsenic oxide (III) we typically use 6.2 moles of butyl alcohol + 3.3 moles of n-heptane (see Table 1 on effects of small variations). The organic mixture can be used for re-extraction of arsenic (III) from a new portion of the oxide mixture, giving the process a cyclic character—a notable feature resulting in a method both economically viable and environmentally benign.

Hydrolysis is a known as a characteristic reaction for all esters. We have decided to investigate hydrolysis of the organic phase containing tri-n-butyl arsenite without separation of the component compounds into individual states. As a result of water treatment of the extract, arsenic oxide (III) is separated—rather than the H_3AsO_3 acid:

$$2(C_4H_9O)_3As + 3H_2O \rightarrow As_2O_3\downarrow + 6C_4H_9OH \tag{4}$$
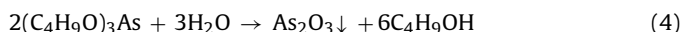
Infrared spectroscopy confirms the absence of antimony oxide in the precipitate. The yield of arsenic oxide is high and ranges between 90 and 93%. Of no less importance is the concurrent generation of the corresponding alcohol and heptane with a 91–94% yield as an azeotropic mixture for re-use in subsequent extractions. Note that the extraction ratio of arsenic is also dependent upon the proportion of alcohol and heptane; see again Table 1.

4. Conclusions

Thus, a new method of separation of arsenic (III) and antimony (III) oxides has been developed. Our method is based on the fact that As_2O_3 treated with a mixture of butyl alcohol and heptane is quantitatively dissolved in the organic phase producing tributyl arsenite. Sb_2O_3 quantitatively remains on the reactor bottom. Subsequent hydrolysis of tributyl arsenite produces arsenic oxide.

Arsenic and antimony are considered contaminants in many ores. The method described here provides a solution for separation of these metals without air contamination that accompanies high temperature roasting—and without huge energy costs of roasting. Thus, the method is potentially much more economical than existing approaches. In general, one finds development of more and more ingenious methods of removal or separation of metals, often as ions. Thus, Barrera et al. [12] have developed a method of removal of chromium ions present in mine drainage by using *Ectodermis* of *Opuntia*. Gamma-radiation polymerized Zn methacrylate has been used as a sorbent for removal of lead ions from wastewater [13]. Some of us use also polymeric flocculating agents for removal of metal suspensions from wastewater [14–16].

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