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The Precipitation of Barium Bromate from a Homogeneous Water–Organic Solvent Solution Containing Strontium

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Abstract

A new and general method of inducing a precipitation from homogeneous solution has been applied to the separation of barium and strontium. The precipitation of barium bromate, a water-soluble compound, is brought about by a gradual change in the composition of the solvent media. An organic compound, such as methanol or tetrahydrofuran, is allowed to diffuse into the original water solution, thus slowly converting the solution into a water–organic mixture. Strontium bromate is about 40 times more soluble in water than barium bromate. The increased solubility plus the greater stability of the strontium MEDTA chelate tend to hold the strontium in solution. The chief advantage of this method over the precipitation of barium chromate is in the preparation of barium compounds. Usually barium must be separated from the chromate before proceeding. However, barium bromate can be easily converted to the oxide, eliminating this separation step.

INTRODUCTION

The classical precipitation methods of separating barium from strontium use chromate (*1*). The use of other insoluble barium compounds has met with limited success. The soluble compounds of barium and strontium have not been studied in a precipitation process. Among the soluble compounds of barium and strontium, the bromates appeared to be the most suitable for a separation process. Strontium bromate is about 40 times more soluble than barium bromate (*2*).

The difference in formation constants of the barium and strontium chelates of MEDTA (1,2-diaminopropanetetraacetic acid) is about 400 (*3*). When both the solubility and formation constant values are used in a complementary way, a reasonable separation appeared to be possible.

The precipitation of the water-soluble barium bromate is brought about by gradually changing the solvent media. An organic compound such as methanol or tetrahydrofuran is slowly introduced into a stirred water solution of barium, strontium, and bromate, thus gradually converting the solution into a water–organic mixture and decreasing the solubility of barium bromate. The strontium tends to be selectively held in solution by the chelating agent as the barium gradually precipitates from solution.

EXPERIMENTAL

Procedure

One millimole of barium and 1 mmole of strontium are added to a 250-ml beaker. Then 0.9 mmole of MEDTA and 10 mmoles of sodium bromate are added and the pH adjusted to about 5.5. The volume is adjusted to 50 ml. No precipitate is present at this point. A 50 or 75 ml volume of methanol or tetrahydrofuran is introduced into the water solution. (This can be done by diffusion, the water solution and the pure methanol or pure tetrahydrofuran sitting side by side in a closed and agitated container, or by slow dropwise addition of methanol or tetrahydrofuran to the stirred water solution.) Barium bromate precipitates slowly from solution. The precipitate is filtered off using a medium porosity porcelain crucible.

Analysis

The determination of strontium in the precipitate and barium in the filtrate was made using the Perkin-Elmer 303 Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

This study is the first application of a general method of inducing the precipitation of water-soluble compounds from homogeneous solution

(*4*). Precipitation is brought about gradually by changing the composition of the media in which the reactants are dissolved.

A water-soluble organic compound with a fairly high vapor pressure, such as methanol, acetone, or tetrahydrofuran, is allowed to diffuse in a closed system, so that the vapor will come into contact with a water solution containing the reactants. With agitation, the solution is gradually and smoothly converted into a water–organic mixture as the organic vapor dissolves and is then mixed throughout the solution.

Comparable results were obtained by adding the organic solvent dropwise to the stirred solution. Although this type of addition is not a true precipitation from homogeneous solution, the character of the precipitate and the results of the separation were very similar. The advantage of the dropwise addition is that exact amounts can be added and the time of inducing a precipitation can be cut drastically from the time needed for diffusion.

Among the variables studied in this system were the usual ones, concentration of the various reagents, pH, and temperature, as well as the following: the type of organic solvent, the ratio of water to the organic solvent in the final solution, and volatilization of the organic versus dropwise addition.

In order to make the study manageable, several of these variables were limited. Only three of the many possible organic compounds were studied. These were fundamentally different structures: an alcohol, a ketone, and an ether. There was some difficulty with the reproducibility with all three organic solvents. The use of acetone produced results that fluctuated randomly and sometimes drastically. However, the fluctuations encountered with methanol and tetrahydrofuran were considerably less than those using acetone. The use of acetone was discontinued because of the failure to achieve reproducibility.

A further improvement in the random fluctuation problem was realized by using the dropwise addition of organic solvent to the water solution rather than volatilization of the solvent. Volatilization is theoretically more advantageous for it does bring about conditions that closely approach a true precipitation from homogeneous solution, but dropwise addition is overwhelmingly more practical. The results using both methods of addition are essentially the same.

The effect of temperature was studied to a limited extent. Some solutions were chilled to about 3 °C in order to bring about further precipitation of the barium bromate. This was accomplished but at the expense of a much higher coprecipitation of strontium. For example, 94% of the barium can

TABLE 1

Line	Number of determinations	% Sr in precipitate	% Ba in filtrate	Organic compound	Ratio, organic:H_2O	Final solution temperature	MEDTA (mmoles)	pH
A	8	0.2–0.3	~6	THF	1:1	23	0.9–1.1	5.5
B	3	0.3	1–5	THF	0.5–2.0:1	23	0.9	5.5
C	4	0.7–2.2	2.5–9	THF	2:1	23	0.9	5.5
D	4	0.7–1.8	2.5–2.8	THF	1:1	3	0.9	5.5
E	6	0.3–0.7	2.6–5.4	THF	1:1	3	Absent	5.5
F	4	0.4–0.9	1.4–5.0	THF	1:1	3	Absent	6–9
G	4	0.3–1.1	1.8–4.3	CH_3OH	1.5–2.0:1	23	0.9	5.5
H	9	0–2.0	2.5–13	CH_3OH	1:1	23	0.9	4–7
I	6	0.7–2.2	~6	CH_3OH	1:1	3	0.9	6–9
J	4	0.6–0.8	4.6–12	CH_3OH	1:1	3	Absent	6–9
K	3	0.4–1.4	2.8–3.9	CH_3OH	1:1	3	Absent	5.5

be precipitated with less than 0.3% of the strontium (see Table 1, Lines A and D). If these solutions are chilled to about 3 °C before filtering, better than 97% of the barium can be precipitated, but correspondingly, slightly over 1% of the strontium coprecipitates.

The amount of MEDTA present in solution has a noticeable effect on the separation. If more than the stoichiometric amount of MEDTA needed to chelate strontium is added, the barium will tend to be held in solution. Without any MEDTA present the coprecipitation of strontium is increased at room temperature. MEDTA was added at about 90% of the stoichiometric amount of strontium and appears to be a satisfactory compromise.

The effect of pH was not as critical as had been expected. When the starting solution was adjusted to about pH 5.5, results were obtained that were as good or better than results at any other pH value.

The effect of excess sodium bromate on the precipitation was also investigated. An excess of 8 mmoles of bromate in 50 ml of solution was needed to bring about the maximum precipitation of barium. Further excess gave no noticeable improvement. Both methanol and tetrahydrofuran gave comparable results with the excess sodium bromate.

A study was also made of the ratio of organic solvent to water in the final solution. Both methanol and tetrahydrofuran showed a distinct leveling off of the percent of barium precipitated at about a ratio of one to one. The tetrahydrofuran had less barium left in the filtrate for the same set of conditions as when methanol was used (see Table 1, Lines F and J).

This study is a preliminary look at an extremely broad area of investigation that may result in the more efficient separation of water-soluble inorganic compounds. The chief value of this study is in demonstrating that water-soluble compounds can now be used in precipitation operations. A wide assortment of separations may be achieved using compounds that were formerly considered unsuitable for precipitation work.

The use of this technique is not limited to water-soluble inorganic compounds. By reversing the process (adding water to an organic solution) the separation of water-insoluble organic compounds can be accomplished. This organic application has even greater possibilities than the inorganic separations.

The main advantage afforded by this method is in the preparation of barium compounds. From an equal molar mixture of barium and strontium, about 94% of the barium can be recovered as the bromate, about 99.7% pure with respect to strontium. The barium bromate can be easily converted to the oxide, thys making the preparation of other barium compounds quite simple.

The barium chromate method (*1*) does give barium that is about 99.95% pure with respect to strontium, but necessitates the separation of barium from chromate before a compound of barium can be made.

From the data in Table 1, the effect of MEDTA at 3°C appears to be minimal. However, at 23°C the MEDTA does appear to influence the coprecipitation of strontium favorably. The lowest value obtained for strontium coprecipitation was that of Line A, Table 1. If the strontium in the filtrate is to be used further, the purity of the strontium can be increased by chilling the filtrate to about 3°C; see Line D. More than half the barium in the filtrate can be removed with about 1 to 2% of the strontium. The remaining strontium will then be about 97% pure with respect to barium.

The weight of the precipitates obtained using this method fluctuated considerably. For example, in eight determinations made under identical conditions, the weights of the precipitates, after being placed in an oven at 110°C for an hour, were scattered between 358 to 398 mg. Undoubtedly some moisture was still present, but the chief source of the weight fluctuation appears to be the coprecipitation of sodium bromate.

Data on the solubility of the barium, strontium, and sodium bromates in various ratios of water to organic solvent were not available. There was a further lack of information about other equilibria in the water–organic solution that beclouded any clear idea of how to proceed advantageously. This made the study exceptionally difficult, often necessitating a trial and error approach.

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