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The Effect of a Nonionic Surface Active Agent on the Coprecipitation of Potassium with BaSO₄

A. M. FORD AND L. W. MARPLE¹

Abstract. Studies were made of the effect of potassium concentration on the amount of potassium coprecipitation with BaSO₄, and the effect of a surface active agent, Triton-X 100, on the coprecipitation of potassium with BaSO₄. It was found that a log-log plot of concentration of KCl in the solution phase vs the amount of potassium coprecipitated was linear indicating that the Freundlich adsorption isotherm was followed. This indicated that the amount of potassium coprecipitated was determined by adsorption on crystalline BaSO₄.

The addition of Triton-X 100 reduced the coprecipitation of potassium by as much as 20% but the improvement was limited by micellar formation at a Triton-X 100 concentration of approximately 0.3%.

In the past, methods for removing the interferences caused by the coprecipitation of foreign ions have generally been approached from the standpoint of removal of the interfering ions. Up to this time the best method of removing interferences has been through ion exchange. Fritz and Freeland (1-3) found that concentrations of potassium twice that of the sulfate ion gave about -6.6% error, and that most other cations interfered to some extent. Cations can be removed through ion exchange. Anions were found to interfere in the decreasing order PO₄⁼, F⁻, NO₃⁻, Cl⁻, Br⁻, ClO₄⁻. An alumina column can be used for both anion and cation separation. Alumina has a high affinity for SO₄⁼, a somewhat lower affinity for PO₄⁼, and F⁻, and a much lower affinity for Cl⁻, NO₃⁻, ClO₄⁻, and most metallic cations. Furthermore sulfate is easily eluted with hydroxide ion.

The main weaknesses of ion exchange separations are 1) cations that form complex ions with sulfate (Cr and Zr.) are not completely removed from solutions, and 2) sulfite is adsorbed and eluted with sulphate on the alumina column.

Hakoila and Noponen (4) studied the effects of various ions on the volumetric determination of sulfate and suggested a blank procedure in which the barium solution was standardized against a solution of high, known concentration of salt. Salt was added to the sample until it was of twice the molar concentration of the sulfate in the sample and the sample titrated. The relative titration error using this technique was about 1.5%. They were able to improve the endpoint by using a Thorin-Methylene blue mixture and adding thorium nitrate to make the endpoint more distinct, but the absolute error remained the same.

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It is the purpose of this study to investigate an untried approach to the problem of coprecipitation with BaSO_4 , the physical protection of the precipitated BaSO_4 crystals from contact with interfering ions by use of a surface active agent. If the coprecipitation phenomenon is due to surface adsorption then the surface active agent should compete with the coprecipitated ion for surface sites on the BaSO_4 crystals and thereby lower coprecipitation. Potassium ion was chosen for study since it is strongly coprecipitated with barium sulfate.

EXPERIMENTAL

The Determination of the Amount of Coprecipitated Potassium

Various amounts of KCl were weighed into beakers and 200 ml of 0.02 M. H_2SO_4 were added. The solution was brought to boiling and 26 ml of 0.2 M BaCl_2 was added at the normal flow rate of the buret, about 50 ml/min. The solutions were digested for four hours and filtered on a clay filtering crucible with three washings with 10% HCl. The BaSO_4 precipitate was transferred to a porcelain crucible, dried, and ignited at the full heat of a meeker burned for fifteen minutes. 0.3000g. samples of the precipitated BaSO_4 were dissolved and the amount of potassium determined with a Baird Atomic internal standard type flame photometer.

Dissolution of Barium Sulfate

Three times the EDTA required to complex the barium present was dissolved in 35 ml of ammonium hydroxide. A weighed amount of BaSO_4 was placed in a beaker, 500 ml of water added, the solution stirred and large particles of BaSO_4 broken up. The suspension was then brought to a boil and the EDTA solution added. Usually 0.2 or 0.3 g samples of BaSO_4 in 500 ml of water required 0.7 g. of EDTA dissolved in 35 ml of ammonium hydroxide. About 45 minutes to an hours boiling was necessary to dissolve the precipitate. The solutions were cooled and transferred to 500 ml volumetric flasks for the final determination with the flame photometer. The samples were further diluted by one-third when the lithium internal standard was added.

Photometric Determination of Potassium

The Baird Atomic flame photometer used was of the internal standard type requiring a 100 ppm Li internal standard. Standard solutions were made up from standard 10,000 ppm Li and standard 10,000 ppm K solutions. The standards were within $\frac{1}{2}$ ppm of each reading used. The calibration curve was linear between 0.1 and 10 ppm.

Density of Triton-X 100

A five ml volumetric flask was weighed and then filled to volume with Triton-X 100 and reweighed. The density was 1.066 g./ml at 255°C.

Hot Precipitation with Digestion

Weights of Triton-X 100 corresponding to 0, 0.01, 0.1, 0.3, 0.5, 0.8, 1.0, and 5.0% by weight of the total solution were weighed into 500 ml beakers with 0.7456 g. KCl and 100 ml of 0.02 M. H_2SO_4 was added. The samples were then heated to boiling and 13 ml of 0.2 M BaCl_2 added. The samples were filtered on a porous bottom crucible, transferred to a porcelain crucible and ignited on a meeker burner for 15 minutes. The ignited BaSO_4 sample was cooled, a weighed amount dissolved, and the potassium determined on a Baird Atomic flame photometer.

Cold Precipitation without Digestion

Weights of Triton-X 100 corresponding to 0, 0.01, 0.1, 0.3, and 0.5% by weight of total solution were weighed into 600 ml beakers with 0.7456 g KCl and 100 ml 0.02 M H_2SO_4 added. 13 Ml 0.2 M BaCl_2 was slowly added and the solution centrifuged. The supernatent liquid was decanted off, the BaSO_4 sample was washed three times with 10% HCl, placed in a porcelain crucible and ignited on a meeker burner. The ignited BaSO_4 sample was cooled, and the potassium determined *vide ante* with a Baird Atomic flame photometer.

Hot Precipitation without Digestion

Weights of Triton-X 100 corresponding to 0, 0.01, 0.1, 0.3, and 0.5% by weight of total solution were weighed into 600 ml beakers with 0.7456 g KCl, and 100 ml 0.02 M H_2SO_4 added. The samples were heated to boiling and 13 ml 0.2 M BaCl_2 added. The supernatent liquid was decanted off, the BaSO_4 sample was washed three times with 10% HCl placed in a porcelain crucible and ignited on a meeker burner. The ignited sample was cooled and the potassium determined as before.

Hot Reverse Precipitation without Digestion

Weights of Triton-X 100 corresponding to 0, 0.01, 0.1, 0.3, and 0.5% by weight of total solution were weighed into 500 ml beakers with 0.7456 g KCl, and 100 ml 0.02 M H_2SO_4 was added. 13 Ml 0.2 M BaCl_2 was placed in a 600 ml beaker and warmed. A sample of H_2SO_4 was heated to boiling and added to the hot BaCl_2 solution through a separatory funnel equipped

with a capillary to slow the flow rate. The samples were then cooled, centrifuged, washed three times with 10% HCl, transferred to a porcelain crucible and ignited on a meeker burner for 15 minutes. The samples were cooled and put in a desiccator. A weighed amount of precipitate was then dissolved and the potassium determined as before.

Cold Reverse Precipitation

Weights of Triton-X 100 corresponding to 0, 0.01, 0.1, 0.3, and 0.5% by weight of total solution were weighed into 500 ml beakers with 0.7456 g KCl, and 100 ml M H₂SO₄ was added. 13 ml 0.2 M BaCl₂ was placed in a 600 ml beaker and the H₂SO₄ solution added through a separatory funnel fitted with a capillary to slow the flow rate. The samples were centrifuged, the supernatant liquid decanted off, washed three times with 10% HCl, transferred to a porcelain crucible and ignited on a meeker burner for 15 minutes. The samples were then cooled and put in a desiccator. A weighed amount of precipitate was then dissolved and the potassium determined as before.

Recovery of BaSO₄

Weights of Triton-X 100 corresponding to 0, 0.01, 0.1, 0.3, and 0.5% by weight of total solution were weighed into 600 ml beakers with 0.7456 g KCl, and 100 ml of 0.02 M H₂SO₄ added. The samples were precipitated hot and digested for two hours without any Triton-X 100 being added. The digested samples were filtered on number 42 filter paper. The samples were placed in a crucible, the filter paper charred, and then ignited at the full heat of the meeker burner for 15 minutes in a previously weighed crucible. The crucibles were cooled and weighed.

RESULTS AND DISCUSSIONS

The data obtained from the direct precipitation of BaSO₄ from various concentrations of KCl followed by digestion was plotted on logarithmic graph paper and found to correspond closely to the Freundlich adsorption isotherm as shown in Figure 1;

$$X/m = KC^n/n$$

X = weight of foreign ion coprecipitated in mg.

m = weight of precipitate in G.

C = molar concentration of foreign ion in solution

K, n = constants

The constants K and n were found to have the values 14.1 and 6.5 respectively under the conditions of the experiment. This

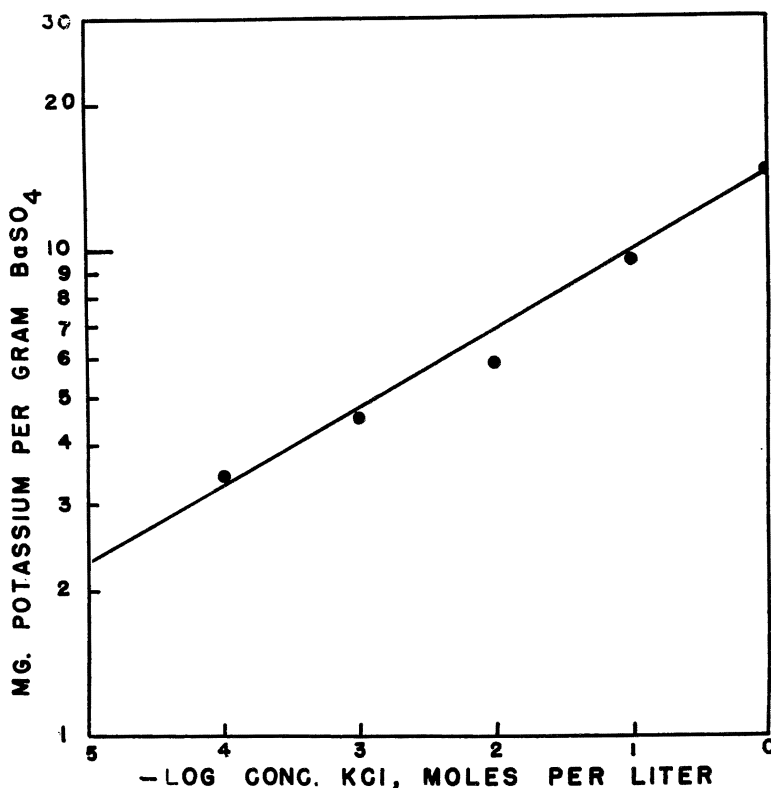


Fig. 1. The coprecipitation of potassium with BaSO_4 precipitated from various concentrations of KCl.

strengthens the conviction that the amount of coprecipitation is determined by the amount of surface adsorption.

The results of the potassium analyses for all of the various treatments are presented in Figure 2.

The solubility of Triton-X 100 in water limited measurements to surfactant concentrations less than 1%. As sulfuric acid solutions of Triton-X 100 were heated up to boiling a white turbidity appeared. This turbidity was caused by a sudden decrease in the solubility of the Triton-X 100 with temperature increase (5). Triton-X 100 owes its solubility in water to the coordination of water molecules to the polyether chain. At temperatures above 60°C , solutions of Triton-X 100 become turbid due to dehydration and subsequent association of molecules into larger colloidal aggregates. Alkali metal salts decrease the solubility of Triton-X 100 and increase the association of molecules into larger aggregates. A micellar growth is suspected to accompany this salting out effect although it was earlier reported by Gonick and

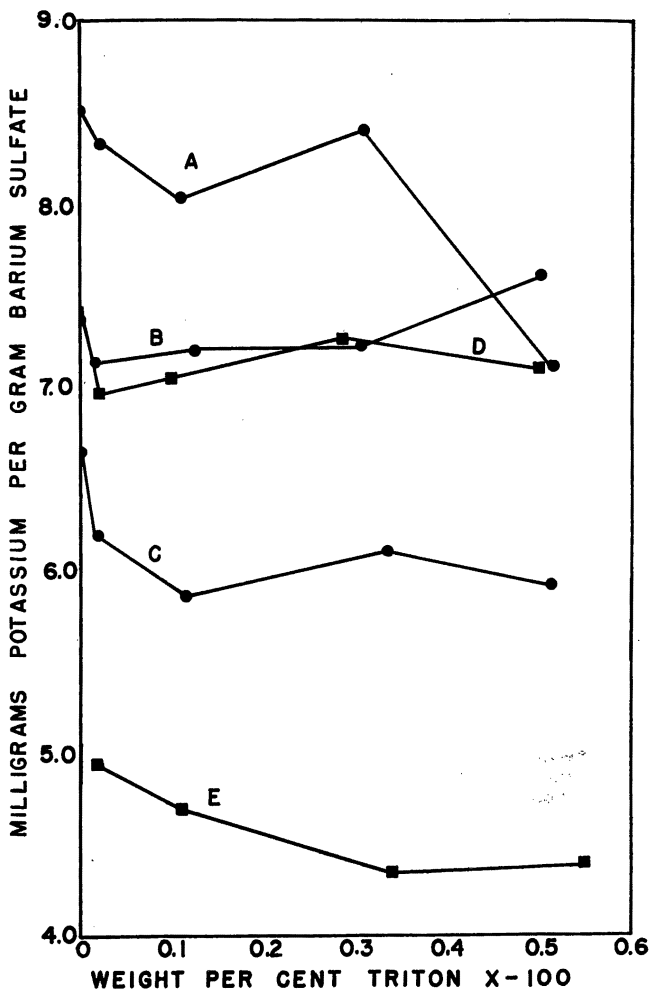


Fig. 2. Coprecipitation of potassium with BaSO₄
 A. Hot precipitation without digestion
 B. Hot precipitation with digestion
 C. Cold precipitation without digestion
 D. Cold reverse precipitation without digestion
 E. Hot reverse precipitation with digestion

McBain that the addition of KCl to a similar surfactant did not cause any deviation of the freezing point depression from its theoretical value. Gonick and McBain also reported the concentration of micelle formation to be 0.0009 M. or about 0.06% by weight. Kushner and Hubbard in a later study found no specific concentration of micellar growth but that the concentration of molecularly dispersed species increased up to 0.3% by weight.

In this study the addition of Triton-X 100 decreased by from

10 to 20% the amount of potassium coprecipitated up to a Triton-X 100 concentration of 0.3% in all treatments except the reverse precipitation with no digestion and the hot precipitation with digestion. Since the maximum concentration of molecularly dispersed Triton-X 100 occurs in a 0.3% solution and the effect of added KCl is to increase the micelle formation, this is in the region where the maximum concentration of Triton-X 100 should be found. This suggests that a surfactant can compete with potassium acting as counter ion in seeking surface sites on BaSO₄ precipitates. Although the least coprecipitation of potassium occurs with reverse precipitation, the coprecipitation of anions is important here. The effect of Triton-X 100 on anion coprecipitation has not yet been determined.

Future experiments should investigate two avenues of approach, first the reverse precipitation procedures in the presence of surface active agents and second the effect of other surface active agents, including both ionic and nonionic surfactants, on coprecipitation with BaSO₄.

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Cation Exchange Equilibria in Mixed Solvents Sorption Characteristics of Common Metals from Water-Dimethyl Sulfoxide-Hydrochloric Acid Mixed Solvent

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Abstract. The systematic study of sorption of Ca, Cd, Co(II), Cu(II), Fe(III), Hg(II), In(III), La, Mn, Ni(II), Th(IV), Pb, Yb, U(VI), and Zn by Dowex 50 x 8 cation exchange resin from dimethyl sulfoxide-water-hydrochloric acid mixed solvent is presented. The sorption characteristics are much the same as those found for acetone-water-hydrochloric acid mixed solvent. Major differences occur in the case of Fe(III), Ca, Mg, and Pb. Many useful separations involving these elements are indicated.

Over the past few years, interest in mixed solvent systems for ion exchange separations has increased significantly. We noted that the water-dimethyl sulfoxide mixed solvent system had not

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