

The Coprecipitation of K^+ and Fe^{3+} with Barium Sulphate

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Abstract

The amounts of K^+ and Fe^{3+} coprecipitated with barium sulphate are investigated as a function of K^+ and Fe^{3+} concentrations. It is found that

$$\log[K^+]_{BaSO_4} = 0.28 \log[K^+]_{soln}$$

over a concentration range of over 3 orders of magnitude which extends up to 28 mol per cent K^+ in $BaSO_4$, with no indication of deviation as concentration increases. Iron, on the other hand, is carried up to about 11 mol per cent, with a clearly indicated maximum. The mutual interference between K^+ and Fe^{3+} is found likewise to differ. The presence of iron in solution markedly depresses the coprecipitation of potassium, especially at $[Fe] > 10^{-3}$ M. Potassium on the other hand, has no effect on the coprecipitation of iron in the $BaSO_4$. These results clearly indicate that the mechanisms of coprecipitation are different for the two ions, and are in agreement with the conclusion expressed elsewhere that potassium forms a mixed crystal with $BaSO_4$, while iron is present as a separate phase, either adsorbed or occluded.

Introduction

The notorious carrying of impurities by barium sulphate has long been recognized as a serious problem in analytical chemistry, particularly in the gravimetric determination of sulphate [1]. This property of barium sulphate has been exploited by many workers [2–4] to isolate many of the heavy elements, in particular thorium, from aqueous solutions.

During the course of work in this laboratory studying the coprecipitation of thorium with barium sulphate, it has been noted that the carrying of thorium is nearly complete if a sufficient amount of monovalent cations is present in solution. In particular, K^+ was found to have the greatest effect, confirming the results of Sill and Willis [2] and of Ambe and Lieser [5]. Burk and Wiles [6] have also confirmed earlier observations [2] that the thorium

recovery is suppressed as increasing amounts of trivalent and quadrivalent ions are present in the precipitation solution.

Although the effects of the thorium coprecipitation have been studied, the coprecipitation of K^+ and Fe^{3+} , ions which are commonly found in environmental water samples, with barium sulphate has not been investigated thoroughly. Geyer and Winzer have studied the coprecipitation of K^+ [7] and Fe^{3+} [8] with barium sulphate but did not report concomitant physical and chemical changes in the solid phase.

Recent work in this laboratory with variously doped $BaSO_4$ precipitates has revealed that various physical and chemical properties of barium sulphate are affected by the presence of potassium but not by the presence of iron. For instance it has been found that the presence of potassium in $BaSO_4$ affects isotopic exchange characteristics [9] as well as surface area, crystal habit, X-ray diffraction patterns, and Raman spectral properties [10]. These changes have been interpreted as manifestations of potassium–barium sulphate mixed crystal formation [7, 10, 11]. The rather minimal effects of the presence of Fe^{3+} in the $BaSO_4$ precipitate on the above properties has been interpreted as being due to the inability of the iron to form mixed crystals with $BaSO_4$ and that its state may be one of adsorption or occlusion [8, 10].

The work presented here reports the results of a quantitative study of coprecipitation of potassium and of iron with $BaSO_4$, and of the mutual influence of potassium and of iron on the coprecipitation of each other.

Experimental Section

Reagents

All reagents used were of reagent grade and were used without further purification. All stock solutions were filtered using 0.45 μ m membrane filters (Gelman DM-450).

Tracer solutions of ^{42}K were prepared by dissolving neutron-irradiated solid KNO_3 (analytical grade) in 0.1 M HNO_3 . The solid samples of KNO_3 (0.1 g and 1.0 g) were irradiated in the SLOWPOKE

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reactor at AECL Commercial Products Division in Ottawa for 1 hour with a neutron flux of 5×10^{11} neutrons $\text{l cm}^{-2} \text{s}^{-1}$. The radiochemical purity of the $^{42}\text{KNO}_3$ solution was verified by gamma spectroscopy which showed all radiocontaminants were short-lived and had decayed to background levels less than 30 min after the time of irradiation.

The $^{59}\text{Fe}^{3+}$ tracer was obtained from Atomic Energy of Canada Limited and had a specific activity of 9 mCi/mg Fe. This was diluted in 0.1 M HNO_3 to give the standard reference solution.

The experiments were performed in a manner such that a standard thorium determination procedure used in our laboratory [6] was simulated. This enabled us to estimate the amount of K^+ and Fe^{3+} ions which could be carried during a typical thorium determination.

To 100 ml of 0.1 M HNO_3 , 1 ml of a 1 mg Ba^{2+} /ml solution was added along with the desired amounts of K^+ and Fe^{3+} cations (as the nitrate) and a known amount of the respective tracer. The beaker was suspended in a water bath held constant at $25.0 \pm 0.1^\circ \text{C}$. The contents of the beaker were stirred using a Teflon impeller at a constant 900 revs per min. Barium sulphate was precipitated by the drop-wise addition of 2.0 ml of 9 M H_2SO_4 . The crystals were filtered using a $0.45 \mu\text{m}$ membrane 30.0 min after the addition of the sulphuric acid. The crystals were then washed with 0.1 M HNO_3 and then with distilled water.

The gamma spectra were recorded using a 3 in \times 3 in Na(Tl)I crystal scintillation spectrometer system. Pulses from the photomultiplier were passed through a preamplifier to a multichannel pulse height analyzer (Northern Scientific NS-900). Radiochemical recoveries were calculated by comparing the radioactivity in the BaSO_4 crystals with the radioactivity of a dried aliquot of the appropriate reference tracer solution.

In some cases, the potassium and iron content of the precipitates was analyzed using atomic absorption spectroscopy. In these cases 10 mg of Ba^{2+} (instead of 1 mg) was precipitated using the same procedure as previously described. The crystals were then dissolved in a mixture of HF and HNO_3 . The resulting solution was analyzed for potassium and iron by atomic absorption spectroscopy (Bondar-Clegg Ltd., Ottawa).

Results and Discussion

Coprecipitation of Potassium

The coprecipitation of potassium ions with barium sulphate as a function of potassium ion concentration in the precipitation solution is shown in Fig. 1. For convenience, the amount carried has been normalized to the amount of BaSO_4 formed, assuming complete

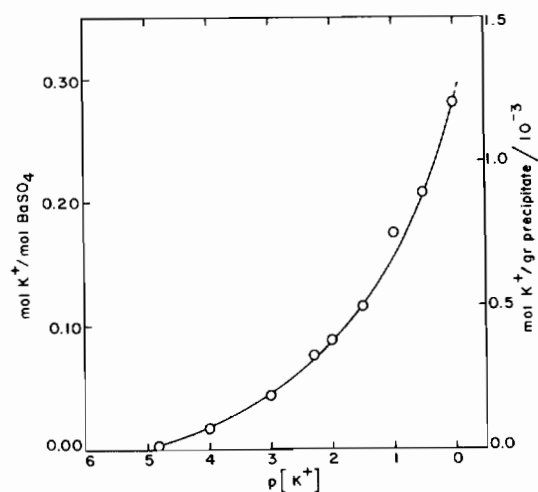


Fig. 1. Amount of K^+ carried by BaSO_4 (10 mg Ba^{2+} per 100 ml of solution) as a function of K^+ concentration. Samples were analyzed using atomic absorption spectroscopy.

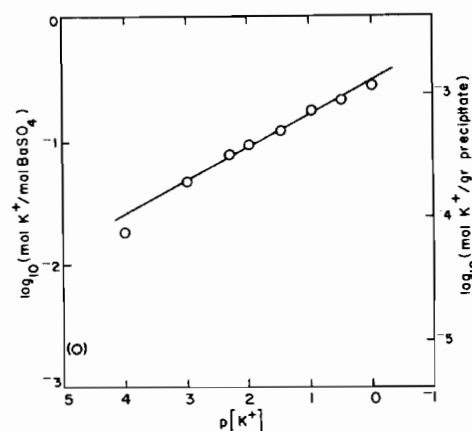


Fig. 2. Logarithmic plot of the amount of K^+ carried vs. amount of K^+ in solution. The conditions are the same as those in Fig. 1.

precipitation. These results are analogous to those of Winzer and Geyer [7], but cover a wider concentration and indicate that under the experimental conditions used, a mol ratio of $\text{K}:\text{Ba}$ up to at least 0.28 can be obtained in the precipitate. A logarithmic plot of the amount of potassium carried vs. the amount in solution shows essentially a straight line which again does not suggest a limit to the amount of potassium carried for the concentration range studied (Fig. 2).

From these data, it can be seen that over a considerable concentration range, the following relationship holds:

$$\log(\text{mol K}^+ \text{ in solid}) = C \log(\text{mol K}^+ \text{ in solution})$$

where C is a proportionality constant. It is seen from Fig. 2 that $C = 0.28$ when $[\text{Ba}^{2+}]$ in solution is 10 mg per litre. This leads us to a logarithmic distribution law [13]:

$$\log \left\{ \frac{\text{mol}[K^+]}{\text{mol}[Ba^{2+}]} \right\}_{\text{solid}} = \lambda \log \left\{ \frac{\text{mol}[K^+]}{\text{mol}[Ba^{2+}]} \right\}_{\text{solution}}$$

considering the amounts of Ba^{2+} in the solid and solution are constants since complete precipitation and negligible solubility effects are assumed. This suggests a continuously renewed equilibrium even though the precipitation is only an approach to equilibrium rather than the equilibrium itself [13]. It also suggests that the potassium is being incorporated into the barium sulphate lattice since the distribution law above is consistent only with the isomorphous replacement or anomalous-mixed-crystal formation categories [13, 14].

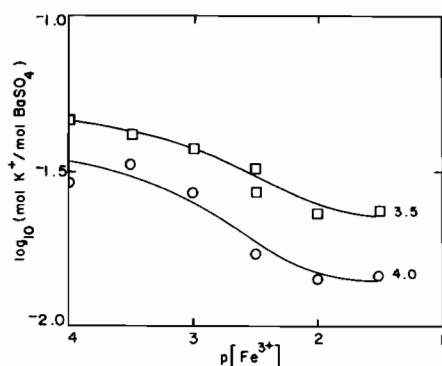


Fig. 3. Amount of K^+ carried by $BaSO_4$ (1 mg Ba^{2+} per 100 ml of solution) as a function of Fe^{3+} concentration. ^{42}K was used as the tracer. Numbers on the Figure give the values of pK^+ in the solution.

Tracer studies using ^{42}K have shown (Fig. 3) that the presence of ferric ions in solution suppresses the carrying of potassium. At this point it is unclear why ferric ions have this effect. One possibility is that the ferric ions and the potassium ions compete for sites in the electrical double layer. With ferric ions in the double layer, the approach of a potassium ion is deterred owing to repulsive electrostatic forces so that the effect is one of competing for initial adsorption sites. On the other hand, one may argue that the presence of the foreign ions will change the rate of $BaSO_4$ precipitation and in this way affect the observed carrying of ions for short times. Fig. 4 illustrates this point as the amount of barium sulphate (measured as the per cent recovery of $^{133}Ba^{2+}$) precipitated in a given short time is plotted vs. the solution concentrations of K^+ and Fe^{3+} ions. To enhance the observable effect, the precipitates were filtered 5 min after the addition of the sulphuric acid (instead of the usual 30 min). According to Burk's data [12], barium sulphate is completely precipitated up to a pM ($M = K^+, Fe^{3+}$) value of 1.5 after 30 min. This indicates that the effect shown in Fig. 4 is one of precipitation rate. The slow growth of barium sulphate in the presence of Fe^{3+} ions could account for the low carrying of K^+ ions.

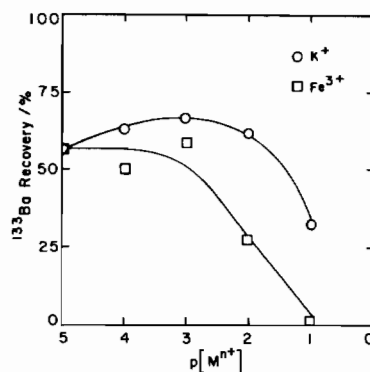


Fig. 4. The radiochemical recovery of ^{133}Ba as $BaSO_4$ as a function K^+ and Fe^{3+} concentration for a precipitation time of 5 minutes.

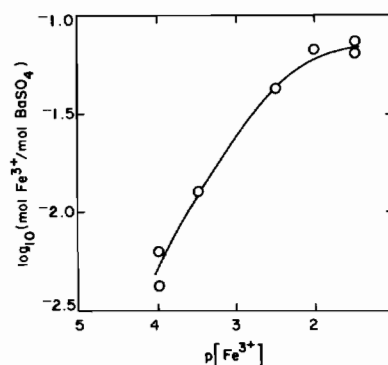


Fig. 5. Logarithmic plot of the amount of Fe^{3+} carried by $BaSO_4$ (1 mg Ba^{2+} per 100 ml of solution) vs. the amount of Fe^{3+} in solution. ^{59}Fe was used as tracer.

Coprecipitation of Iron(III)

Preliminary results using $^{59}Fe^{3+}$ tracer have given indication of saturation with respect to the amount of iron carried by the precipitate within the same cation concentration range as was used for the potassium study. This is shown by the logarithmic plot in Fig. 5 where the essentially straight line at lower Fe^{3+} solution concentration reaches a plateau by a concentration of 10^{-2} mol l^{-1} . These results are typical within the potassium concentration range between $pK = 4.0$ to 1.5. The limit is more clearly seen in Fig. 6 where the experimental conditions are slightly different (*i.e.* 10 mg of Ba^{2+} is used instead of 1 mg). The data in Fig. 6 give an estimated limit of 0.11 for the $Fe:Ba$ mol ratio. It is clear that Fe^{3+} coprecipitates with barium sulphate in a manner different from that of potassium and that more potassium may be carried than iron (approximately 3 times more).

It is interesting to note that the presence of potassium does not affect the coprecipitation of iron. This was shown by the invariance of the amount of iron carried in experiments like that of Fig. 5 when plotted for several potassium concentrations and particularly by Fig. 7 which plots the amount of Fe^{3+}

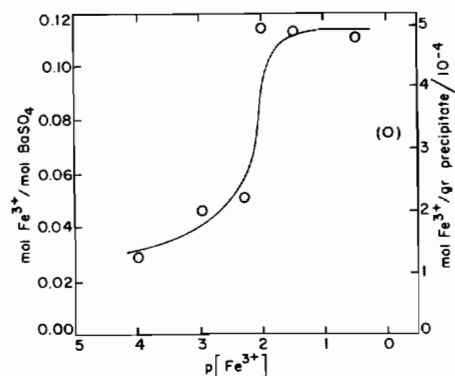


Fig. 6. Amount of Fe^{3+} carried by BaSO_4 as a function of Fe^{3+} concentration. The samples were analyzed using atomic absorption spectroscopy. The amount of Ba^{2+} used was 10 mg per 100 ml of solution.

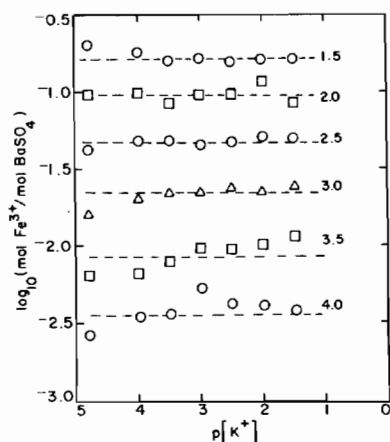


Fig. 7. Amount of Fe^{3+} carried by BaSO_4 as a function of K^+ concentration. The conditions are the same as those in Fig. 5. ^{59}Fe was used as the tracer.

carried vs. the potassium concentration for several Fe^{3+} concentrations. The horizontal lines generated by such a plot show no observable effect of the K^+ ions.

The iron coprecipitation seems to follow an isotherm in which an approach to a limit is seen. This suggests that we are observing the results of adsorption processes, or that the iron has low, limited solubility within the precipitate. Further evidence presented elsewhere [8, 10] indicates that the iron is not incorporated into the barium sulphate lattice to a large extent, but is rather present in a separate state.

The effect of a highly charged cation such as Fe^{3+} has been shown to suppress the carrying of K^+ ions but not the reverse. Burk and Wiles [4] have shown that there is an increase in the surface area of barium sulphate when precipitated in the presence of potassium ions. It has also been shown [10] however that Fe largely counteracts this effect. Thus the coprecipitation is not inconsistent with surface adsorption of

Fe on the BaSO_4 . Further evidence [10] drawn from changes in the Raman spectrum of the SO_4^{2-} ion indicates that the K^+ and Fe^{3+} have quite different interactions with the crystal lattice: the K^+ is seen to form a solid solution in the BaSO_4 while the Fe^{3+} appears to form a separate phase independent of the BaSO_4 and presumably adsorbed on its surfaces (or occluded).

Summary

It has been shown that K^+ ions coprecipitate with barium sulphate to a greater extent than do Fe^{3+} ions for equal cation concentrations in the precipitation solution. Furthermore, a limit as to the amount of iron coprecipitated was observed whereas no such limit was present in the potassium coprecipitation curves even at K concentrations as high as 1 M. This is interpreted as being due to different coprecipitation mechanisms for each cation rather than ionic strength effects. There also seems to be a competition between K^+ and Fe^{3+} ions as the presence of Fe^{3+} in solution is seen to suppress K^+ coprecipitation slightly. The presence of K^+ in solution is seen neither to suppress nor to enhance the iron coprecipitation. The Fe^{3+} effects seem to be kinetic in nature and likely do not reflect an equilibrium.

Acknowledgements

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