Studies on the Separation of Alkaline Earth Elements. IV. Coprecipitation of Barium in the Induced Precipitate of Lead Sulfate

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In the preceding paper⁽¹⁾ the precipitation of lead sulfate induced⁽²⁾ by the barium ion was studied by means of turbidimetry, and it was shown experimentally that there were several relations among the quantities of substances involved. The present paper reports the ratio of coprecipitation of barium measured radiometrically by use of ^{140}Ba as a tracer, and the amount of induced precipitate of lead sulfate measured amperometrically⁽³⁾. Freundlich's equation of adsorption isotherm⁽⁴⁾ was found to be applicable to the experimental results obtained. It is understood that this induced precipitation furnishes a method of concentration of small amounts of barium in the presence of large amounts of lead.

Experimental

Reagents. — Lead nitrate, guaranteed grade, 0.482 M, aqueous solution.

Barium chloride, 0.005 M/l; Aqueous solution of guaranteed grade salt was mixed with a suitable amount of a hydrochloric acid solution of carrier free $^{140}BaCl_2$.

Ammonium acetate, 10.23 M/l (pH≈6.22); prepared from ammonia water and acetic acid, both of which were of guaranteed grade.

Apparatus. — SHIMADZU pen — recording polarograph for amperometry.

SHIMADZU glass electrode pH meter for pH measurement.

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1) M. Shinagawa and T. Murata, *J. Science Hiroshima Univ., Series A*, **18**, 429 (1955).

2) F. Feigl. "Spot Tests", Vol. 1. Elsevier Publishing Co., (1954), p. 204.

3) I. M. Kolthoff and J. J. Lingane, "Polarography", Interscience Publishers, Inc., New York, N. Y. (1952), p. 913.

4) H. Freundlich, *Z. physik. Chem.*, **57**, 385 (1907).

Kobe Kogyo End Window G. M. Counter (131 Type. Thickness of the mica window was 3.1 mg./cm^2.) and stainless steel cupped planchets with 2.5 cm. diameter were used for the radioactivity measurements.

Procedure and Results.

1) Determination of the amounts of precipitated barium and lead.—In order to know the quantity of coprecipitated barium with lanthanum fluoride, Gest et al. reported the dilution method[5], while the authors prefered the following method. The specific activity of β-ray of the remaining barium labeled with ^{140}Ba in the supernatant solution was measured and compared with that of the standard solution. Two ml. of either solution was almost evaporated in a cupped planchet under an infrared lamp and less than 0.8 ml. of 0.5 M sulfuric acid was added to make the lead sulfate layer uniform which had a thickness of 18 mg./cm.^{2} This way of preparation facilitated good reproducibility of the counting. Since the solutions labeled with ^{140}Ba usually contain the daughter, ^{140}La, they had been kept more than 20 days after their preparation before the specific activities were measured.

The quantity of precipitated lead ions was also determined indirectly, measuring the lead ions in the supernatant solution by the amperometric titration with potassium chromate solution at -1.0 V of fixed potential.

2) The amount of coprecipitated barium as a function of aging time.—Into a stoppered Erlenmeyer flask, 500 ml. of a mixed solution (pH 5.50) containing 0.096 M lead nitrate, 2.07 M ammonium acetate (The molar ratio of ammonium acetate to the lead ion was chosen as in the previous paper[1].), and 2×10^{-4} M barium chloride, was placed and stirred well after the addition of 7.50 ml. or 12.5 ml. of 0.5 M sulfuric acid. The flask was kept in a 20±0.05°C thermostat.

At regular intervals 5 ml. batches of solution were taken out of it and centrifuged. The specific activities of the supernatant solution told the amount of the precipitated barium removed at intervals as shown in Fig. 1. It was found that the percentage of coprecipitation remarkably increased within the first half an hour and remained almost constant thereafter.

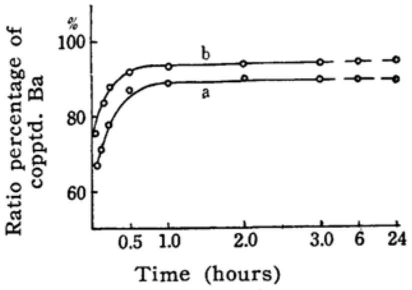

Fig. 1. The amount of coprecipitated barium as a function of aging time.
Solution: Pb(NO$_3$)$_2$ 0.096 M.
CH$_3$COONH$_4$ 2.07 M.
Ba^{++} 1×10^{-4} M.
To 500 ml. of the solution 7.50 ml. (Curve (a)) or 12.50 ml. (Curve (b)) of 0.5 M H$_2$SO$_4$ was added, aged at 20°C.

3) The precipitations as a function of the amount of sulfuric acid added.—As mentioned in section 2, 40 ml. of the mixed solution was taken into a 100 ml. stoppered Erlenmeyer flask, and 0.50—5.00 ml. of 0.5 M sulfuric acid was added at a rate of 7—8 sec./ml.

It was stirred well and kept being aged at 20°C. After 2 hours it was centrifuged and analysed. Fig. 2 illustrates the results when the coexisting barium concentrations were 0 M, 1×10^{-4} M and 2×10^{-4} M Ba^{++}. Table 1 (A) shows the data of the last case.

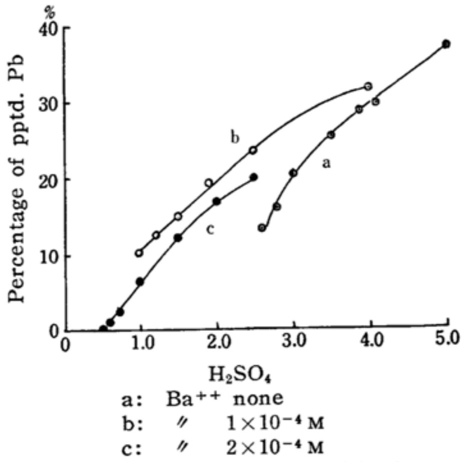

Fig. 2. Precipitation ratio of lead as a function of the amounts of sulfuric acid added.
Solution: Pb^{++} 800 mg/40 ml., CH$_3$COONH$_4$ 2.07 M, pH 5.50.
0.5 M H$_2$SO$_4$ was added. Aged for 2 hours at 20°C.

TABLE I (A)

AMOUNTS OF SULFURIC ACID AND THE PRECIPITATES

Solution: 800 mg. Pb^{++} and 1098 γ Ba^{++} in 40 ml of 2.07 M CH$_3$COONH$_4$. 0.5 M H$_2$SO$_4$ was added, aged for 2 hours at 20°C.

H$_2$SO$_4$ added ml.	Ba copptd. γ	Ba copptd. %	Pb pptd. mg.	Pb pptd. %	ratio of pptd. (Ba)/(Pb) γ/mg.
0.50	94_3	$85._9$	$3._2$	0.4	236
0.60	94_9	$86._4$	$4._8$	0.6	198
0.80	103_6	$94._4$	$18._4$	2.3	57
1.00	104_2	$94._9$	$40._8$	5.1	26
1.50	105_3	$95._9$	$96._0$	12.0	11
2.00	106_4	$96._8$	$130._4$	16.3	8
2.50	106_8	$97._3$	$156._0$	19.5	7

(Mean values of three data.)

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[5] H. Gest, N. F. Ballov, B. M. Abraham and C. D. Coryell, "Radiochemical Studies; Fission Products", McGraw-Hill Book Co., Inc., New York, Paper **12**, 145 (1951).

TABLE I (B)

Solution: 1600 mg. Pb^{++} and 1098 γ Ba^{++} in 40 ml of 4.14 M CH_3COONH_4, 0.5 M H_2SO_4 was added, aged for 2 hours at 20°C.

H_2SO_4	Ba		Pb		ratio of pptd.
added ml.	copptd. γ	copptd. %	pptd. mg.	pptd. %	(Ba)/(Pb) γ/mg.
1.50	101_3	$92._3$	$52._8$	3.3	192
2.00	103_4	$94._2$	$52._8$	3.3	195
3.00	104_3	$95._0$	$147._2$	9.2	71
4.00	105_3	$95._9$	$241._6$	15.1	43
5.00	106_0	$96._5$	$320._0$	20.0	33
7.00	108_5	$98._8$	$320._0$	20.0	34
10.00	109_6	$99._8$	$588._8$	36.8	19

(Mean values of three data.)

As can be seen from Fig. 2, when barium was absent lead ions were not precipitated until 2.60 ml. of sulfuric acid was added, because of the masking effect of acetic acid radical. Since in the presence of barium the precipitate appeared by the addition of less than 2.60 ml. of sulfuric acid, it was possible to regard this as induced precipitation owing to the presence of barium.

In the case of Table 1 (A), 86—96% of barium was coprecipitated with 20% of lead precipitate, while 92—99% of barium with less than 20% of lead in the case of double concentrations of lead ions and ammonium acetate as shown in Table I (B). In this case lead sulfate was not precipitated until 7.50 ml. of sulfuric acid was added, in the absence of barium. Therefore, the more concentrate the lead ion, the greater the readiness with which lead sulfate was induced to precipitate. The amount of coprecipitated barium increased significantly with the increase in lead sulfate precipitate, while the ratio of barium to lead in the precipitate decreased noticeably.

Results

1) The precipitation as a function of the initial concentration of barium. — A mixed solution as prepared in section 2 was used, having several concentrations between 6.86 and 68.6 mg. barium per liter. To each 40 ml. batch of these solutions were added 1.00 and 1.30 ml. of sulfuric acid as the representing amounts of the acid necessary for the induced precipitation taken by the preliminary experiments shown in Fig. 2 curve a and c, and it was then let stand for 30 min. in a thermostat to equilibriate the precipitate as in section 2. Table II (A) and (B) show the data of the experiments.

TABLE II (A)

INITIAL CONCENTRATIONS OF BARIUM AND THE PRECIPITATES

Solution: 800 mg. Pb^{++} in 40 ml. of 2.07 M CH_3COONH_4. 1 ml. of 0.5 M H_2SO_4 was added, aged for 30 min. at 20°C.

Initial Ba	copptd. Ba		pptd. Pb		ratio of pptd. (Ba)/(Pb)
γ	γ	%	mg.	%	γ/mg.
279	24_4	$87._9$	$28._8$	3.6	8.4
549	48_7	$88._7$	$35._2$	4.4	13.8
1098	97_3	$88._6$	$42._4$	5.3	22.9
1647	145_4	$88._3$	$50._4$	6.3	28.8
2196	198_1	$90._2$	$58._4$	7.3	33.9
2745	249_0	$90._7$	$72._8$	9.1	34.2

(Mean values of three data.)

TABLE II (B)

The same conditions as in (A), but 1.30 ml. of H_2SO_4

Initial Ba	copptd. Ba		pptd. Pb		ratio of pptd. (Ba)/(Pb)
γ	γ	%	mg.	%	γ/mg.
279	25_3	$92._1$	$87._2$	10.9	2.9
549	50_6	$92._2$	$92._8$	11.6	5.4
1098	98_6	$89._5$	$100._8$	12.6	9.7
1647	146_0	$88._7$	$112._8$	14.1	12.9
2196	198_3	$90._3$	$138._4$	17.3	14.3
2745	250_3	$91._2$	$146._4$	18.3	17.0

(Mean values of three data.)

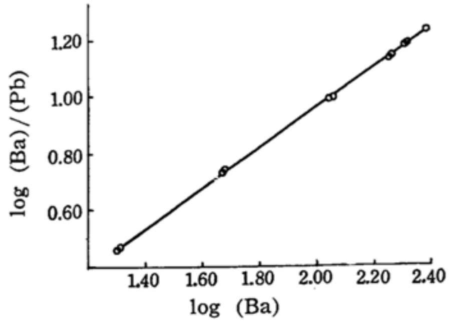

Fig. 3 (A) Logarithmic relation between ppt. ratio and final barium concentration.
Solution: Pb^{++} 800 mg./40 ml., CH_3COONH_4 2.07 M.
1.00 ml. of 0.5 M H_2SO_4 was added, aged for 30 min. at 20°C.

From Table II where the amount of sulfuric acid is constant, it can be seen that in the presence of more barium ions, more lead sulfate precipitates, while the percentage of coprecipitation of barium is unchanged with the initial concentration of barium in the solution; i. e. 89—90% in the case of (A) and 89—92% in (B).

In Fig. 3 (A) and (B), linear relationship between the logarithmic value of precipitation ratio ((Ba)/(Pb) in γ/mg., in Tables II (A) and (B)) and that of the concentration of barium in the final solution equilibriated with the precipitate (C in γ/40 ml.). Therefore, these relations

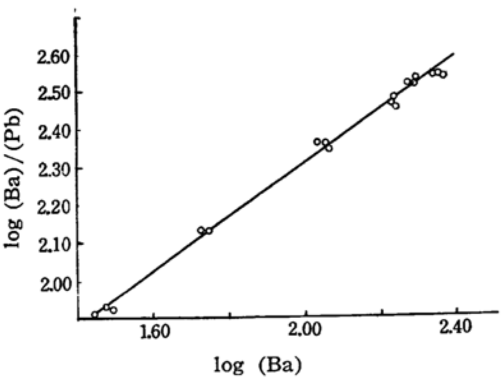

Fig. 3 (B) Conditions were the same as (A), but 1.30 ml. of H_2SO_4 was added.

are expressed by the Freundlich's adsorption isotherm,

$$(\mathrm{Ba})/(\mathrm{Pb}) = aC^{1/n}$$

Where a and n are the constants which can be calculated from the intercepts and the inclination of the linear relations; $a=2.63$ and $n=1.38$ in (A) while $a=0.30$ and $n=1.38$ in (B). The value of a is larger in (A) than in (B), indicating that the adsorbability of barium is greater in (A) than in (B); in other words the smaller the amount of sulfuric acid added, the relatively larger the amount of coprecipitated barium. The n values in both cases are identical, indicating that the natures of the adsorption phenomena are of the same quality.

2) *Precipitations from the solution without ammonium acetate.*—When there was no ammonium acetate, the masking agent for lead ions, the ordinary lead sulfate precipitation was observed. It was not regarded as a precipitation induced by barium sulfate. The experimental results can be seen in Table III.

It was found from Table III that the percentage of the coprecipitated barium without induced lead sulfate was about 32—48%, which was much lower than that with the induced precipitate, i. e. about 85—99%.

TABLE III

THE PRECIPITATIONS WITHOUT INDUCTION

Solution: 800 mg. Pb^{++} and 549 γ Ba^{++} in 40 ml., 1.5 ml. of 0.5 M H_2SO_4 was added, aged for 30 min. at 20°C.

copptd. Ba		pptd. Pb		ratio of pptd. (Ba)/(Pb)
γ	%	mg.	%	γ/mg.
17_0	$31._7$	$8._0$	1.0	42.5
18_4	$33._5$	$20._0$	2.5	9.2
21_1	$38._5$	$40._0$	5.0	5.3
22_0	$40._0$	$60._0$	7.5	3.6
24_0	$43._8$	$80._0$	10.0	3.0
26_6	$48._4$	$100._0$	12.5	2.7

(Mean values of three data.)

Conclusion

On adding 0.5 M sulfuric acid, 0.096 M lead in 2.07 M ammonium acetate solution is precipitated inductively in the presence of 0.5—5×10^{-4} M barium ion.

The amount of the coprecipitating barium follows the Freundlich's adsorption isotherm. The adsorption equilibrium is obtained within 30 min. after the addition of sulfuric acid. The adsorption percentage is greater as the amount of sulfuric acid added decreases in the range of possible amount of producing the lead sulfate.

The amount of coprecipitating barium is not the function of the amount of lead sulfate precipitate; it is almost constant, (85—99%) being much greater than that in the absence of ammonium acetate.

Further investigations with more elaborated experimental conditions are expected to get an excellent method of separation of a small amount of barium from a large amount of lead.

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