of gelatin as in the absence of gelatin. This result shows that Ostwald ripening is of no, or of subordinate, significance under the aging conditions described in the paper.

6. The magnitude of the surface of a year-old precipitate has been determined by Paneth's method using radioactive chloride as an indicator.

7. Indication has been obtained that the amount of bromide removed from the solution corresponds to exchange in the surface layer only, if the values obtained upon shaking of silver chloride in the presence of wool violet are extrapolated to a zero time of shaking.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA AND THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Determination of the Specific Surface of Barium Sulfate

BY I. M. KOLTHOFF AND W. M. MACNEVIN

In a previous publication[1] methods have been described for the determination of the distribution coefficient K of thorium B between the surface of barium sulfate and solutions in water or in 50% ethanol. Knowing the value of K the same methods can be applied to the determination of the specific surface of arbitrary samples of barium sulfate

$$\mathrm{Ba_{surface}} = \frac{\mathrm{ThB_{surface}}}{\mathrm{ThB_{solution}}} \times \frac{\mathrm{Ba_{solution}}}{K}$$

From the practical viewpoint the method involves certain disadvantages. In the first place it requires equipment for the radioactive measurements. In the determination of the distribution of thorium B between the surface and the solution, the fraction of the thorium B entering the lattice as a result of recrystallization has to be taken into account. This recrystallization complicates matters, particularly when dealing with fresh, imperfect precipitates. Finally the amount of barium in solution has to be known under equilibrium conditions. If the barium sulfate investigated is imperfect and impure, and contains coprecipitated barium or sulfate, as is often the case, the amount of barium added to the solution may change during the experiment and should be determined in the sample when analyzed for thorium B.

In a discussion of exchange adsorptions on the surface of barium sulfate[2] it was mentioned that the following reaction can be made use of in the determination of the specific surface

$$\underset{\text{Surface}}{\mathrm{Ba^{++}SO_4^{=}}} + \underset{\text{Solution}}{\mathrm{CrO_4^{=}}} \longrightarrow \underset{\text{Surface}}{\mathrm{Ba^{++}CrO_4^{=}}} + \mathrm{SO_4^{=}}$$

The following relation holds when equilibrium is attained in the surface

$$\frac{\mathrm{CrO_4^{=}}_{\text{surface}}}{\mathrm{CrO_4^{=}}_{\text{solution}}} = K\,\frac{\mathrm{SO_4^{=}}_{\text{surface}}}{\mathrm{SO_4^{=}}_{\text{solution}}}$$

K being equal to 1.1 at 25°.[2]

With imperfect products of barium sulfate the exchange upon shaking with solutions containing sulfate and chromate is not limited to the surface layer only, because there is recrystallization. Upon extrapolation of the "time–adsorption" curve to a time of shaking of zero, the amount of chromate exchanged in the surface is found when the product does not recrystallize too rapidly. The method has distinct advantages over the "radioactive" one, because it is easily carried out and slight impurities of sulfate or barium in the barium sulfate have hardly any effect upon the results. Moreover, a rapid and simple method has been developed, according to which the magnitude of the surface was found from the amount of wool violet adsorbed when the surface was saturated with the dye. The use of wool violet 4BN for the determination of the specific surface of lead sulfate has been described before.[3] In the latter case the same amounts of wool violet were found to be adsorbed from solutions containing either slight excess of sulfate or of lead. In the case of barium sulfate such a simple relation was not found to hold.

Preparations Used

Wool Violet 4BN.—Several samples were obtained from the National Aniline and Chemical Company and purified by methods described previously. The sodium content was found to be 4.04%, although in the earlier work the sodium content was found to be 5.85–6.0% (theoretical

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[1] I. M. Kolthoff and W. M. MacNevin, THIS JOURNAL, **58**, 725 (1936).

[2] I. M. Kolthoff and G. E. Noponen, *ibid.*, **59**, 1237 (1937).

[3] I. M. Kolthoff, W. von Fischer and Charles Rosenblum *ibid.*, **56**, 832 (1934).

5.75%). In spite of six more recrystallizations, the sodium content remained the same and did not reach the theoretical value. It finally appeared that the dye contained small amounts of aluminum (0.1–0.3%) and traces of iron which could not be removed by any recrystallization process, although the conditions were varied widely. As far as adsorbability is concerned the dye behaved in a similar way to the sample used in the lead sulfate work. Although the colorimetric method is very suitable for the determination of the dye, it could not be used in cases when the centrifugate, after the adsorption, was slightly turbid. For this reason an empirical chemical method was developed. The following procedure gave reproducible results and was found to be more accurate than the colorimetric method. Ten milliliters of the dye solution, containing 0.5–5.0 mg. of dye is mixed at 25° with 25 ml. of 0.02 *N* permanganate and 10 ml. of 4 *N* sulfuric acid and allowed to stand without disturbance for thirty minutes. Excess of potassium iodide is then added and the iodine titrated with 0.02 *N* sodium thiosulfate solution; 1 ml. of 0.02 *N* permanganate was found to be equivalent to 0.280 mg. of dye.

Dye solutions containing 100 mg. of wool violet or more per liter formed a precipitate slowly when the barium concentration in the solution was greater than 0.001 molar. Therefore, in the adsorption experiments a large excess of barium salt in the solution should be avoided, although it was found that in barium sulfate suspensions the precipitation was hardly significant even when the barium concentration was 0.0025 molar. It was noticed that dye solutions containing small amounts of barium chloride foamed strongly on shaking whereas no foaming was observed in the absence of barium salt. A similar behavior was found in barium sulfate suspensions containing dye, which foamed only when barium chloride was present.

Barium Sulfate.—The preparation of two samples of barium sulfate, designated as "A" (fine product) and "B" (coarse product, perfected at 175°) has been described by us previously.[4] Both products were used in the present study. In addition other samples were prepared.

Product C.—To a solution of 24 g. of anhydrous sodium sulfate (c. p.) in 240 ml. of water was added at room temperature with vigorous mechanical stirring a solution of 40 g. of barium chloride dihydrate in 240 ml. of water. The amount of sulfate was about 3% in excess of the amount required to precipitate the barium. The suspension was transferred quickly to 250-ml. bottles and centrifuged for five minutes. The supernatant liquid was poured off immediately, 150 ml. of water was added, the bottles shaken mechanically until all the precipitate was suspended and then centrifuged again. This washing process was repeated eight times, after which no turbidity for sulfate was obtained in the supernatant liquid. The precipitate was then washed twice with 50% ethanol, once with 95% ethanol and twice with absolute ethanol, filtered with suction, placed in an oven at 50° for four hours and stored in a sulfuric acid desiccator.

Whereas products A and B were well aged, the product C was still very fresh and imperfect. Moreover, the latter product contained sodium sulfate which was given off very slowly upon shaking with aqueous solutions. The thorium B method is not suitable for the determination of the specific surface for the reasons mentioned before. A great number of experiments was carried out by the radioactive method, but the results were not reliable.

Product D.—This was obtained by heating product C for twenty-four hours at 400°.

Product E.—This was obtained by heating product C for twenty-four hours at 500°.

Experimental

Adsorption of Wool Violet on the Fine $BaSO_4$ "A".—A given volume of dye solution of known concentration was shaken for a definite period of time with a given weight of the adsorbent. The suspension was then centrifuged until clear and samples were taken for the determination of the final dye concentration. The shaking period varied between fifteen minutes and five hours and it was found that equilibrium was attained after thirty minutes of shaking. In the following work one hour of shaking was used throughout.

The results obtained with the fine product "A," using 50 ml. of dye solution, except in the first 8 experiments in which 25 ml. was used, are reported in Table I and shown graphically in Fig. 1.

TABLE I

ADSORPTION OF WOOL VIOLET BY "FINE" BARIUM SULFATE "A"

$BaSO_4$, g.	Wool violet concn., mg./l.		$BaCl_2$ molar	Na_2SO_4 molar	Mg. dye adsorbed per g. $BaSO_4$
	Orig.	Final			
0.100[a]	25	3.9			5.3
.100[a]	50	25.3			6.2
.200[a]	100	45.0			6.9
.200[a]	200	141			7.4
.200[a]	200	138			7.8
.300[a]	300	202			8.2
.400[a]	400	274			7.9
.500[a]	500	343			7.8
.100	50	19.7	0.001		15.1
.100	100	64	.001		18.0
.200	200	114	.001		21.5
.400	400	225	.001		21.9
.500	900	674	.001		22.6
.400	1000	783	.0025		27.1
.400	800	585	.0025		26.9
.200	600	490	.0025		27.5
.200	400	295	.0025		26.2
.100	50	40		0.0001	5.0
.200	100	78		.0001	5.50
.200	100	90		.001	2.50
.500	400	351		.001	4.90
.500	900	844		.001	5.60

[a] 25 ml. of dye solution used.

The behavior of barium sulfate with the dye is different from that of the lead sulfate. In the latter case the same amount of dye was found ad-

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[4] I. M. Kolthoff and W. M. MacNevin, THIS JOURNAL, **58**, 499 (1936).

sorbed on the saturated surface, whether a suspension of the lead sulfate was taken in water or in 0.001 molar lead or in 0.001 molar sodium sulfate. With barium sulfate no saturated surface was obtained in 0.001 molar sodium sulfate even at a dye concentration as high as 900 mg. per liter, although the amount adsorbed approaches the value obtained in the saturated surface when a dye solution in water was used. In the latter case the surface was found to be saturated at a final dye concentration in the solution of 0.14 g. per liter, the amount of dye adsorbed being 7.8 mg. per 1 g. If this saturated surface corresponds to a monomolecular layer of dye adsorbed, the saturated surface in 0.001 molar barium chloride should correspond to a trimolecular layer (22.0 mg. per gram). In 0.0025 molar barium chloride the amount of dye adsorbed in the saturated surface was found to be slightly greater (27 mg. per gram) than that in 0.001 molar barium solution. This difference might be attributed to a precipitation of a slight amount of the barium salt of the dye, although the constancy of the amount adsorbed with increasing dye concentrations in the solution seems to contradict this conclusion.

The following experiments were made with the barium sulfate "B," the surface of which was about 50 times smaller than of product "A." Five grams of the product was shaken with 25 ml. of a solution of wool violet using a saturated solution of barium sulfate in water or with 50 ml. of a dye solution in 0.001 molar barium chloride. The results are given in Table II.

TABLE II

ADSORPTION OF WOOL VIOLET ON COARSE BARIUM SULFATE "B 175°C."

Wool violet concn., mg./l.		$BaCl_2$ concn., molar	Mg. of dye adsorbed per 1 g. of $BaSO_4$
Orig.	Final		
100	79		0.10
200	162		.19
300	264		.18
400	359		.20
400	346	0.001	.67
500	447	.001	.66
600	546	.001	.67

For the fine product the ratio of the amounts of dye adsorbed in the saturated surface from saturated barium sulfate solution and 0.001 molar barium chloride was found to be 7.8/22.0 = 0.35; for the coarse product it was found equal to 0.20/0.67 = 0.30. The agreement is very satisfactory, considering the small surface of the coarse product. From microscopic measurements the specific surface of the coarse product "B" was calculated and found to correspond to 1.0×10^{18} barium ions in the surface of 1 g. of barium sulfate. From a saturated barium sulfate solution 0.2 mg. of dye was adsorbed in the saturated surface corresponding to 1 dye ion per 6.2 barium ions in the surface. From 0.001 molar barium chloride this relation corresponded to 1 dye ion per 1.9 barium ions in the surface. The ratio of the surfaces of the fine and the coarse products as calculated from the dye adsorption on the saturated surfaces in saturated solution of barium sulfate was found to be 7.8/0.2 = 39, and in 0.001 molar barium chloride 22/0.67 = 33. Considering the possibility of a precipitation of a small amount of the barium salt of the dye from 0.001 molar barium chloride solution, the former value is more reliable although the agreement between the two is very satisfactory.

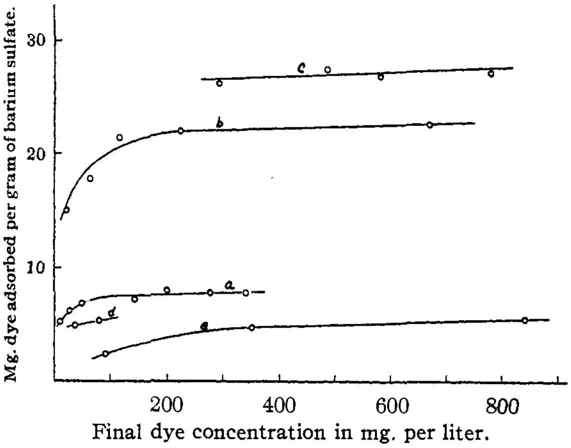

Fig. 1.—Dye adsorption on $BaSO_4$ "A": (a) satd. soln. of $BaSO_4$; (b) in 0.001 *M* $BaCl_2$; (c) in 0.0025 *M* $BaCl_2$; (d) in 0.0001 *M* Na_2SO_4; (e) in 0.001 *M* Na_2SO_4.

The dye adsorption on products C, D and E was determined by shaking 0.1-g. samples for one hour with 25 ml. of a solution containing 0.5 g. of wool violet per liter of saturated barium sulfate in water. It was shown that under these conditions the surface becomes saturated with dye. The following amounts of dye expressed in mg. per gram of barium sulfate were found to be adsorbed: 11.2 (C), 5.7 (D) and 0.75 (E).

Radioactivity Method

The specific surface of Products A and B was determined by the radioactive method, according to the technique outlined in a previous paper.[1] The adsorption of thorium B on product "A" was determined from 50% ethanol. After correction for the amount of barium adsorbed from the solution the surface was found to correspond to 5.2 × 10^{19} barium ions per 1 g. The adsorption of thorium B on product B was determined from aqueous medium, the amount of barium ions adsorbed being negligibly small. From microscopic measurements the surface was calculated to correspond to 1.0 × 10^{18} barium ions per 1 g. The ratio of the surfaces of products "A" and "B" by the thorium B method is found to be equal to 52, and by the dye method to 39. The agreement is very satisfactory. The surface of product "C," determined as that of "A" was found to correspond to 2 × 10^{20} barium ions per gram. This value is too large due to removal of barium ions from the solution by reaction with the sulfate which was present as an impurity in the product.

Chromate Method

As an example, the results obtained with product "A" will be given in detail. Fifty-ml. samples of a solution that was 0.001 *M* in sodium sulfate and 0.001 *M* in sodium chromate were shaken with 0.8-g. portions of product "A" for 15, 30, 60, 120, 180 minutes, respectively. The samples were centrifuged and the supernatant solutions analyzed for chromate by the iodometric method. The amounts of chromate adsorbed after the indicated periods of time were 22.4, 23.2, 23.4, 23.4, and 23.45%, respectively. Extrapolation to a time of shaking of zero yields 23.4% exchange of chromate.

$$[SO_4^{=}]_{\text{surf. eq.}} = \frac{[CrO_4^{=}]_{\text{surface}}\,[SO_4^{=}]_{\text{solution}}}{[CrO_4^{=}]_{\text{solution}} \times 0.8 \times 1.1}$$

$[SO_4^{=}]_{\text{surf. eq.}}$ gives the number of sulfate ions on the surface per gram of barium sulfate after exchange equilibrium is established. The amount of sulfate ions on the surface of the original product is equal to this calculated value plus the number of chromate ions which are on the surface when exchange equilibrium is reached. $[SO_4^{=}]$ in solution is equal to the amount of sulfate ions originally present in the solution plus the amount of sulfate ions which have exchanged with chromate. Thus

$$[SO_4^{=}]_{\text{surf. eq.}} = \frac{0.234\{(5 \times 10^{-5} \times 6.06 \times 10^{23}) + (0.234 \times 5 \times 10^{-5} \times 6.06 \times 10^{23})\}}{0.766 \times 0.8 \times 1.1} = 1.6 \times 10^{19}$$

The number of sulfate ions per 1 g. of the original product $[SO_4^{=}]_{\text{surface}}$ then is equal to 1.6 × 10^{19} + 0.9 × 10^{19} = 2.5 × 10^{19}.

The results obtained with the various products are given in Table III.

TABLE III

SPECIFIC SURFACE DETERMINATION BY THE CHROMATE METHOD

Product	$BaSO_4$ taken, g.	Vol. of $SO_4^{=}$ – $CrO_4^{=}$ soln.[a] ml.	Chromate removed in % after extrapolation to time zero	$[SO_4^{=}]_{\text{surf. eq.}} \times 10^{-18}$ per gram	$[SO_4^{=}]_{\text{surface}} \times 10^{-18}$ per gram
A	0.8	50	23.4	16.3	25
B	.8	10	21.4	0.23	0.39
C	.4	50	28.7[b]	36	58
D	.4	50	17.5	17.3	30.5
E	.4	50	3.0	2.2	2.9

[a] Solution was 0.001 molar in sodium sulfate and 0.001 molar in sodium chromate.

[b] Product highly imperfect; the chromate enters the precipitate fairly rapidly; removed after twenty minutes 22.7%, after one hour 26.6%, after three hours 31.2%, after 21 hours 53%.

Discussion

The calculation of the value of the distribution coefficient of thorium B between the surface of barium sulfate and solution was based upon the microscopic measurement of the "surface average particle diameter" of product B.[1] This was found to be 6.92 microns, corresponding to a surface of 0.19 M^2 per gram. Assuming the particles to be cubic, this value corresponds to 0.96 × 10^{18} barium ions per gram of barium sulfate. The corresponding values of product A were calculated from the distribution of thorium B at equilibrium conditions.

Assuming that the amount of dye adsorbed in the saturated surface of various products of barium sulfate from a wool violet solution in water saturated with barium sulfate is proportional to the specific surface, it is possible to calculate the surfaces and sizes of the various products from the data obtained with product B. An adsorption of 0.2 mg. of dye per 1 g. of barium sulfate corresponds to a specific surface of 0.96 × 10^{18} barium ions and 0.19 M^2 per gram and an average particle diameter of 6.9 microns.

The results obtained by the chromate method yield the number of sulfate ions per gram of barium sulfate and are not based upon the microscopic measurements. Assuming again the particles to be cubic, the average particle diameter and the surface expressed in M^2 per gram can be calculated from the experimental results.

TABLE IV

SPECIFIC SURFACE OF VARIOUS PRODUCTS OF BARIUM SULFATE DETERMINED BY THE THREE DIFFERENT METHODS

a = Number of Ba or SO_4 ions $\times 10^{-18}$ per gram of barium sulfate. b = Surface in M^2. c = Average particle size in microns.

	Product A			B			C			D			E		
Method	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
Wool violet	37	7.4	0.17	1.0[x]	0.19[x]	6.9[x]	54	10.8	0.12	26	5.2	0.25	3.6	0.7	1.8
Chromate	25	5.0	.26	0.39	.078	17.0	58	11.6	.11	30.5	6.1	.21	2.9	.58	2.2
Thorium B	52	10.4	.13	1.0[x]	.19[x]	6.9[x]									

[x] Calculations of wool violet and ThB methods based upon the microscopic measurements.

A summary of all the data is given in Table IV. Considering the limitations of the various methods and the assumptions made it is gratifying to see that the order of agreement of the magnitude of the surfaces calculated by the three different methods is satisfactory.

Product C is highly imperfect, causing an uncertainty in the extrapolated value of the amount of chromate exchanged. The ratio of the surfaces of products A (well aged) and C (fresh) by the chromate method was found to be 0.43, and by the wool violet method 0.69. This fair agreement indicates that the internal surface of the imperfect product C in open communication with the liquid phase is very small indeed. The corresponding ratios of products A and D are 0.82 and 1.4 and of products A and E 8.6 and 10.6, respectively. From a practical viewpoint it appears that the wool violet method is the most suitable one for the determination of the specific surface of fresh and aged products of barium sulfate.

Summary

The specific surface of various products of barium sulfate has been determined by three different methods. The simplest method is based on the determination of the amount of wool violet adsorbed in the saturated surface of barium sulfate. The method based upon the exchange between chromate and sulfate ions in the surface of barium sulfate yields valuable results. The thorium B method is limited to well-aged products of barium sulfate.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

Exchange Adsorption Phenomena with Calcium Oxalate Monohydrate

BY I. M. KOLTHOFF AND E. B. SANDELL

Various examples of exchange between lattice ions in the surface of a slightly soluble precipitate and foreign ions of the same electrical sign in the solution have been found in this Laboratory.[1] In the present paper examples of similar exchanges at the interface of calcium oxalate monohydrate and aqueous solutions of various electrolytes are given. Moreover, it is shown that the saturated solution of calcium oxalate in an electrolyte does not contain equivalent amounts of calcium and oxalate when one of the lattice ions gives an exchange with one of the foreign ions of the solution and the system contains an excess of the solid. The difference between the inequality of calcium and oxalate concentrations increases with increasing amount of surface exposed to the solution, or when dealing with a particular product with increasing amount of solid.

Experimental

Preparation of Calcium Oxalate Monohydrate.—Three products of calcium oxalate monohydrate, prepared as follows, were used in the present work.

Product I.—One liter of hot 0.50 *M* ammonium oxalate solution was added slowly with vigorous stirring to one liter of hot 0.52 *M* calcium chloride solution acidified with one milliliter of concentrated hydrochloric acid. The time of addition of the oxalate solution was ten minutes. The precipitate was washed with redistilled water with the aid of a centrifuge until it was chloride-free. The washed precipitate was suspended in a liter of water, allowed to stand for three days, collected by centrifugation, rewashed and finally mixed with one-half liter of water. The suspension thus obtained was used directly in the adsorption experiments.

Product II.—This product was prepared in the same way as Product I, except that potassium oxalate was used instead of ammonium oxalate in the precipitation.

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[1] For a review see I. M. Kolthoff, *J. Phys. Chem.*, **40**, 1027 (1936); for exchange reactions on the surface of barium sulfate *cf.* I. M. Kolthoff and G. E. Noponen, THIS JOURNAL, **59**, 1237 (1937).