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Exchange Adsorptions on the Surface of Barium Sulfate

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In recent years various examples have been found in this Laboratory of an exchange between an ion in solution and a lattice ion of the same electrical sign in the surface of an ionic lattice.[2] In the present study it is shown that the following exchange adsorptions occur on the surface of barium sulfate

$$\begin{array}{llll} BaSO_4(s) + & Pb^{++} \longrightarrow & PbSO_4 + & Ba^{++} \\ BaSO_4(s) + & CrO_4^= \longrightarrow & BaCrO_4 + & SO_4^= \\ BaSO_4(s) + & 2IO_3^- \longrightarrow & Ba(IO_3)_2 + & SO_4^= \\ \text{Surface} & \text{Solution} & \text{Surface} & \text{Solution} \end{array}$$

In the above cases it was shown conclusively that we were dealing with an exchange. On shaking, for example, a lead chloride solution with barium sulfate, lead, but no chloride, was removed from solution. Moreover, the amount of barium which was found in the solution after the shaking was approximately equivalent to the amount of lead removed. It was found that alkali ions, calcium, chloride and iodide were unable to give exchange with one of the lattice ions in the surface of barium sulfate.

Preparation of Suspension of Barium Sulfate.—In the following manner pure barium sulfate with a relatively large specific surface was obtained. Into 1500 ml. of 1.11 *M* sodium sulfate (238 g. of Merck C. P. product) was poured quickly with stirring 1500 ml. of 1.10 *M* barium chloride (403 g. of Mallinckrodt analytical reagent $BaCl_2 \cdot 2H_2O$). After the precipitate had settled the mother liquor was siphoned off and the suspension transferred to a 12-liter bottle with about 8 liters of distilled water. The bottle and its contents were then placed on a shaker which shook the bottle back and forth about once every second. Every day the bottle was taken off the shaker and after the precipitate had settled the wash water was siphoned off and fresh water added. This procedure was continued for one month. The precipitate was then put into a Pyrex flask with about 4 liters of conductivity water and placed in an oven at 92–95° for one week. In the manner described a drastic aging, accompanied by purification of the barium sulfate occurred, thereby producing a more steady state with regard to the surface of the adsorbent. After the heating period, the water was siphoned off again and about 5 liters of conductivity water was added. The suspension was then allowed to stand with an occasional shaking; the water was replaced once a week for a period of a year before the barium sulfate was used in the adsorption experiments.

Purity of the Barium Sulfate Suspension.—A large amount of the suspension (containing about 10 g.) of barium sulfate and a small amount (about 2 g.) were shaken with 250 ml. of water for twenty-four hours. The suspensions were centrifuged and 200-ml. portions evaporated to a volume of about 15 ml. in the presence of 2 ml. of 0.1 *M* potassium chromate. The barium chromate precipitates were filtered on glass sintered crucibles and after washing several times with water were dissolved in 3 ml. of 6 *N* hydrochloric acid and 20 ml. of water. After addition of potassium iodide the liberated iodine was titrated with 0.001 *N* thiosulfate. The titration volumes for the large and the small amounts of suspension were 4.55 and 4.65 ml., respectively, corresponding to a molar concentration of barium of 0.76×10^{-5} and 0.80×10^{-5}, respectively. The agreement between the two figures showed that neither barium chloride nor sodium sulfate was coming out of the precipitate into the supernatant liquid upon long periods of standing.

Specific Surface of the Barium Sulfate.—The specific surface of the product was compared by the wool violet method with that of other products, the surface of which had been determined with the aid of thorium B[3] and of wool violet. From the dye adsorption from a solution containing no excess of barium a surface of 3.8 M^2 per g. was found. From the adsorption from a 0.0025 *M* barium chloride solution a surface of 3.3 M^2 per g. was found, or as an average 3.5 M^2 per g.

Moreover, the specific surface was determined by a new method in which use was made of the exchange reaction occurring upon shaking barium sulfate with a chromate solution

$$BaSO_4(s) + CrO_4^= \longrightarrow BaCrO_4(s) + SO_4^=$$

The following relation holds when equilibrium in the surface is attained

$$\frac{[CrO_4^=]\text{surface}}{[CrO_4^=]\text{ solution}} = K\,\frac{[SO_4^=]\text{surface}}{[SO_4^=]\text{solution}} \qquad (1)$$

The distribution constant *K* was determined in a separate study[1] the results of which will be communicated soon. The homogeneous distribution of chromate throughout the barium sulfate phase was determined at varying mole percentages of chromate in the solid phase; at 25°, *K* was found equal to 1.1. Assuming that the same value of *K* determines the mixed crystal formation in the surface layer only, $[SO_4^=]$ surface can be calculated from the analytical results with the aid of equation (1). The advantage of this method is that it is not based upon the microscopic measurement of the dimensions of a coarse product of barium sulfate as is the case with the methods referred to.[3]

Twenty-ml. portions of the aged barium sulfate suspension were treated at room temperature with 10 ml. of a solution 0.01 *M* in sodium chromate and 0.01 *M* in sodium sulfate. The suspensions were shaken for various periods of time (Table I), centrifuged and the supernatant liquids

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(1) Part of a thesis submitted by G. E. Noponen to the Graduate School of the University of Minnesota in partial fulfilment of the requirements of the degree of doctor of philosophy, June, 1936.

(2) For a review *cf.* I. M. Kolthoff, *Kolloid Z.*, **68**, 190 (1934); *J. Phys. Chem.*, **40**, 1027 (1936); for another interpretation of the mechanism see also E. J. W. Verwey, *Kolloid Z.*, **72**, 187 (1935).

(3) I. M. Kolthoff and Wm. M. MacNevin, THIS JOURNAL, **58**, 725 (1936).

analyzed for chromate iodometrically. The weight of barium sulfate in each experiment was obtained by evaporating a 20-ml. portion to dryness, heating the residue for twenty-four hours at 130° and weighing. The results are given in Table I.

Table I

Determination of Specific Surface of Barium Sulfate by Chromate Method

Time of shaking, hours	0.25	0.5	1	2
Chromate adsorbed, %	9.3	9.85	11.3	12.1

Although the barium sulfate was well aged, apparently it was still subject to a slow recrystallization process under the above experimental conditions, resulting in an incorporation of the chromate into the recrystallizate upon longer periods of shaking. By extrapolating the figures after one and two hours of shaking to a time of shaking of zero, the amount of chromate having taken part in the surface exchange only is found to be 10.5%. Knowing the composition of the solution and correcting for the amount of chromate which has entered the surface, it is calculated with the aid of equation (1) that 0.31% of the precipitate is surface. The same method was applied to a product of barium sulfate whose specific surface was found to be 2.8 times greater than that of the above by the dye method and 2.7 times greater by the chromate method. The close agreement between these two entirely different methods is very gratifying. Assuming that the barium sulfate particles are cubic it is calculated that a surface extent of 0.31% corresponds to a specific surface of 1.6 M^2 per g. Hence, this method yields a magnitude of surface of the same order as that calculated from the dye adsorption, the latter value being 3.5 M^2 per g., corresponding to 0.68% surface.

Exchange Experiments

Experiments with Lead Iodide.—Three hundred ml. of a saturated lead iodide solution and about 175 ml. of the barium sulfate suspension were pipetted into a volumetric flask of 500 ml., the contents made up with water to volume, the suspension after thorough shaking transferred to a 700-ml. glass-stoppered bottle, shaken for twenty-four hours and centrifuged. The centrifugate was analyzed for lead, iodide and barium. The barium sulfate was collected, dried at 130° and weighed. In the calculation of the amounts adsorbed a correction was applied for the volume of the solid barium sulfate. A blank prepared by diluting 300 ml. of the lead iodide solution to 500 ml. was treated and analyzed in a similar way. Twenty-five ml. portions of the centrifugate and the blank were analyzed for lead in the following way. Two ml. of an ammonium sulfide solution was added and the lead sulfide filtered off and washed quickly. The precipitate was dissolved on the filter in hot 6 *N* hydrochloric acid, and the solution, after washing the filter paper, boiled till hydrogen sulfide was expelled. The solution was neutralized with ammonia, 2 ml. 0.1 *M* potassium chromate was added and the suspension was digested until the lead chromate appeared crystalline. The precipitate was collected and the chromate content determined iodometrically.

Twenty-five ml. portions of the centrifugate and the blank were analyzed for iodide by treating with 5 ml. of chlorine water and allowing to stand for fifteen minutes. The chlorine was expelled by boiling and the iodic acid determined iodometrically.

Two hundred ml. of the centrifugate was analyzed for barium after the lead had been removed as sulfide. The filtrate was boiled to expel the hydrogen sulfide, neutralized and evaporated to a volume of about 15 ml. after addition of 2 ml. 0.1 *M* potassium chromate. The barium chromate was collected and determined iodometrically. In order to know the solubility of barium sulfate in the lead iodide solution of the composition used in the adsorption experiment, 500 ml. was shaken with 0.2 g. of barium sulfate (too little to consider exchange or adsorption) and the barium determined in 200 ml. of the centrifugate by the above procedure.

Using 22.07 g. of barium sulfate and 500 ml. of suspension 0.00084 molar in lead iodide, 6.05 micromoles of lead and 0.39 micromole of iodide were found to be adsorbed per gram of barium sulfate. Hence the adsorption of iodide (probably as lead iodide) is very small as compared with the adsorption of lead, indicating that exchange had occurred between lead and barium in the surface of barium sulfate. This conclusion was substantiated by the results of the barium analysis. The barium concentration after the adsorption was found to be 20.0×10^{-5} molar, whereas in the blank (0.2 g. of barium sulfate) a solubility corresponding to 1.8×10^{-5} molar was found. If all of the lead adsorbed had exchanged with barium a barium concentration in the solution of 26.6×10^{-5} molar is calculated, taking the solubility product of barium sulfate equal to $(1.8 \times 10^{-5})^2$. If the iodide were adsorbed as lead iodide a barium concentration of 25.8×10^{-5} molar is calculated. Considering the relatively great experimental errors when working with such dilute solutions the agreement between the calculated value (25.8×10^{-5}) and the experimental value (20.0×10^{-5} *M*) is satisfactory.

In the above experiments the suspensions were shaken for twenty-four hours. Other experiments were made in which suspensions were shaken for various periods of time with lead iodide solution. The results are given in Table II.

Table II

Adsorption of Lead and Iodide on 10.42 g. Barium Sulfate

Time of shaking	1 hour	24 hours	8 days	43 days
Micromoles of Pb^{++} adsorbed per 10.42 g.	56.6	70.0	93.4	109.0
Micromoles of I^- adsorbed per 10.42 g.	10.7	10.7	10.7	10.7

Evidently the true adsorption of iodide (as lead iodide) occurs very quickly and does not change upon longer periods of shaking than one hour. The amount of lead removed from solution increases with the time of shaking; a similar phenomenon has been described for the adsorption of chromate from a solution containing chromate and sulfate ions. It is attributed to a slow recrystallization of the well-aged barium sulfate with a subsequent incorporation of the lead into the lattice.

Experiments with Lead Chloride.—A c. p. sample of lead chloride was recrystallized twice from dilute hydrochloric acid, well washed and dried. The experiments were carried out in the way described for lead iodide, the concentration of lead chloride in the final suspension being 0.001 molar. The chloride concentration was determined potentiometrically by titrating with 0.01 *M* silver nitrate added from a microburet in a medium containing 50% of acetone. A pronounced jump in potential is obtained at the equivalence point. The precision of this titration at this great dilution is 0.5% or better.

The lead concentration was determined without separating from barium by direct precipitation of the lead as chromate from a medium 0.04 *N* in perchloric acid.[4] Fifty-ml. samples of the centrifugate were treated with 40 ml. of water, 2 ml. of 20% perchloric acid, the mixtures heated to boiling and 10 ml. 0.05 *M* potassium dichromate added. The suspension was digested until the lead chromate became orange in color and had a crystalline appearance. After standing for five to six hours at room temperature the lead chromate was collected and determined iodometrically.

The analysis for barium was the same as described in the case of lead iodide.

Using 14.81 g. of barium sulfate and 500 ml. of suspension 6.05 micromoles of lead and 0.0 micromoles of chloride were found to be adsorbed per g. of barium sulfate after six hours of shaking. Only lead is removed from the solution by exchange with barium in the surface of barium sulfate. Again, a satisfactory agreement was found between the amount of barium in solution and the concentration calculated from the amount of lead having exchanged with barium ions. The barium concentration of the supernatant liquid after the adsorption was found to be 14.8×10^{-5} molar, whereas the calculated value was 17.9×10^{-5} m.

Experiments with Ammonium and Sodium Iodate.—Approximately 200 ml. of barium sulfate suspension and 50 ml. of 0.02 *M* ammonium iodate and enough water to make the volume 500 ml. were pipetted into a volumetric flask of 500 ml. The contents were transferred to a glass-stoppered bottle, shaken for twenty-four hours, whereupon the suspension was centrifuged. A blank was prepared by diluting 50 ml. of 0.02 *M* ammonium iodate to 500 ml. The iodate was determined iodometrically in 25-ml. portions of the centrifugate. The sum of ammonium and iodate was determined in 25-ml. portions of the centrifugate, using the hypochlorite method described by Kolthoff and Stenger[5] for the determination of ammonium. The barium concentration of the centrifugate was determined in the way described in the section on the test of purity of the barium sulfate used. The solubility of barium sulfate in 0.002 *M* ammonium iodate was determined in a similar way after shaking 0.2 g. of barium sulfate in 0.002 *M* ammonium iodate for twenty-four hours, and was found to be 1.32×10^{-5} molar.

Using 25.17 g. of barium sulfate and 500 ml. of suspension 0.002 *M* in ammonium iodate, 1.65 millimoles of iodate and 0.0 millimole of ammonium were found to be adsorbed per 1 g. of barium sulfate. Therefore, no adsorption of ammonium iodate occurred, but only an exchange between iodate and sulfate ions in the surface of barium sulfate.

$$\underset{\text{Surface}}{BaSO_4} + \underset{\text{Solution}}{2IO_3^-} \longrightarrow \underset{\text{Surface}}{Ba(IO_3)_2 + SO_4^=}$$

This conclusion was substantiated by the barium analysis, the barium concentration of the centrifugate being found equal to 0.16×10^{-5} molar. From the amount of iodate exchanged and the solubility product of barium sulfate in 0.002 *M* ammonium iodate $(1.32 \times 10^{-5})^2$, a barium concentration of 0.33×10^{-5} molar is calculated. Considering the experimental difficulties involved in the analysis of such small amounts of barium (part of which is precipitated as sulfate instead of as chromate) the agreement is satisfactory.

The effect of time of shaking upon the amount of iodate removed from solution was investigated next. Using the same experimental conditions as described above, 10.6 micromoles of iodate was found to be adsorbed after one hour of shaking, 12.3 after six hours, 12.7 after twenty-five hours, 31.6 after seven days and 61.9 after forty-two days, per 8.38 g. of barium sulfate. This result was difficult to interpret as it was not expected that the iodate could be incorporated in the barium sulfate in the form of mixed crystals, as in the case with lead or chromate. The experiments were repeated using sodium iodate instead of the ammonium salt. In this case the amount of iodate adsorbed after one hour of shaking was found to be 9.41 micromoles per 7.50 g. of barium sulfate, and this figure remained unchanged even after twenty days of shaking. Apparently a peculiar decomposition occurs upon longer periods of shaking of ammonium iodate solution with barium sulfate.

A series of experiments was carried out which gave evidence that iodate is not incorporated in barium sulfate in the form of mixed crystals. To 30 ml. of 0.1 *M* sodium sulfate were added 25 ml. of 0.1 *M* barium nitrate and 25 ml. 0.097 *M* sodium iodate. After various periods of time samples were centrifuged and analyzed for iodate. The percentages of iodate found in the precipitate after the various periods of time were 1.82 after one-half hour, 1.82 after one hour, 1.82 after five hours, 1.16 after twenty-five hours, 1.00 after ninety-six hours. If mixed crystal formation had occurred, the amount of iodate in the precipitate would be expected to increase with time of shaking, whereas actually a decrease was found.

Experiments with Calcium Iodide and Potassium Iodide.—Using 25.56 g. of barium sulfate in 500 ml. of 0.0025 *M* calcium iodide neither an adsorption of iodide nor of calcium was found after twenty-four hours of shaking. In the case of potassium iodide no adsorption of iodide was found after this time of shaking.

Summary

1. A new method for the determination of the specific surface of barium sulfate which is based upon the exchange between chromate and sulfate ions in the surface of barium sulfate has been described.

2. It has been shown that lead ions exchange with barium ions and iodate with sulfate ions in the surface of barium sulfate.

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[4] D. J. Brown, J. A. Moss and J. B. Williams, *Ind. Eng. Chem., Anal. Ed.*, **3**, 124 (1931).

[5] I. M. Kolthoff and V. A. Stenger, *Ind. Eng. Chem., Anal. Ed.*, **7**, 79 (1935).