

made in a thermostat at 28 (corr.) $\pm 0.01^\circ$. The three or more readings for the same concentration checked to within ± 0.03 ohm. The cell constant, 0.762, was determined at 25° by potassium chloride solution containing 7.4931 g. per 1000 g. of water, using the Kohlrausch standard value.⁴

Results.—The experimental values are given in Table I. When the three values from the "International Critical Tables" which fall within our concentration range are plotted and the equivalent conductance at 28° obtained by interpolation, they agree with the data reported in this paper.

Supported in part by the Rockefeller Fluid Research Fund of the School of Medicine of Stanford University.

Summary

Measurements were made of the conductivity at 28° of a series of aqueous barium hydroxide solutions varying in concentration from 0.016 mole per liter to 0.20 mole per liter.

(4) "International Critical Tables," Vol. 6, p. 230.

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED FEBRUARY 6, 1933

PUBLISHED JULY 6, 1933

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

The Adsorbent Properties and the Specific Surface of Lead Sulfate

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

The method of determining the specific surface of a lead salt in equilibrium with its saturated solution by using Thorium B as a radioactive indicator originated with F. Paneth.¹ It was intended to apply his method to a study of the internal structural changes accompanying the aging of freshly formed precipitates of lead sulfate. However, since we cannot agree with some of the conclusions derived by the above authors from their experimental work, it was decided to make a more extensive study of the specific surface and the adsorbent properties of aged lead sulfate. The results of this study which yielded new information will be described in the following.

Materials Used.—All chemicals were c. p. products and as a rule three times recrystallized from water.

Lead Sulfate.—Coarsely crystalline products were prepared according to the directions of Paneth and Vorwerk.¹ 2 *N* sulfuric acid was added slowly to a solution of 95 g. of lead nitrate in 7 liters of water, the whole being well stirred during the mixing. The precipitate was washed ten times by decantation with 10-liter portions of distilled

(1) F. Paneth, *Z. Elektrochem.*, **28**, 113 (1922); Paneth and W. Vorwerk, *Z. physik. Chem.*, **101**, 445 (1922).

water. One batch (preparation I) was used as such after the final decantation. In the later work it appeared that the product still contained a trace of lead salt adsorbed. Another batch was prepared in a similar way, but after the final decantation it was shaken with 10-liter portions of water for six five-day periods. The centrifugates of the last three shakings yielded a constant lead concentration in the saturated solution of the salt, indicating that adsorbed material was no longer being given off.

Thorium B.—The source of the Th B was a Rd Th preparation with a γ -ray equivalence of 4.1 mg. Ra.² Th B was obtained by exposing platinum foils or wires to the thoron emanating from the Rd Th in a closed chamber in the usual manner. The active deposit dissolved in a saturated solution of lead sulfate in the same medium as that in which the particular experiment was performed.

Experimental Methods

Since lead ions are fairly strongly adsorbed by a glass wall, all the experiments were carried out in paraffin lined bottles closed by paraffined stoppers. In order to avoid adsorption of lead by filtering materials, the separation of the solid was accomplished by means of the centrifuge. Suspensions with known weights of lead sulfate were withdrawn from the stock suspension by stirring the latter with an electrically driven stirrer and pipetting off 100-cc. samples. In order to know the lead sulfate content several analyses were made in which the amount of solid in 100 cc. of the suspension was filtered through Gooch crucibles and weighed after ignition. These determinations gave results reproducible within 1%. The suspensions pipetted out contained approximately 1 g. of lead sulfate per 100 cc. and were concentrated when desired by removing known volumes of the centrifuged supernatant liquid. In the adsorption and the kinetic exchange experiments¹ the samples were shaken on a machine maintained at a speed of 350 to 400 phases per minute with an amplitude of 3.8 cm.

Determination of Thorium B Adsorbed.—About 10 cc. of the Thorium B solution was added to a suspension containing about 24 cc. of solvent. After the indicated time of shaking, the containers were centrifuged and the radioactivity of the supernatant liquid compared with that of the original solution, the latter being diluted to give approximately the same activity as the centrifugate. Activities were determined by evaporating 5-cc. samples of active solutions on a steam-bath and noting the rate at which they discharged a Lind³ interchangeable head electroscope equipped with an aluminum leaf. After performing these measurements, correction was made for the decay of the Thorium B during the course of the observations. For this purpose the decay constant of Thorium B⁴ was taken as 1.82×10^{-5} sec.⁻¹.

Evaporation was effected in circular copper dishes, about 6 cm. in diameter and 1 cm. in depth, all dishes having been spun over the same form to ensure an identical radiating surface. Three samples of each radioactive solution were evaporated and their activities determined.⁵ This procedure permitted a determination of Thorium B removed from the solution to within about 2% of the total adsorption. Blank experiments showed that small amounts of lead nitrate or sodium sulfate in the evaporation residue did not affect the reproducibility of the measurements.

Determination of Dissolved Lead in the Solutions.—The dissolved lead was precipitated as lead chromate, and the latter after filtering and washing was titrated iodometrically. The volume of sample taken for analysis varied with the lead concentration and was chosen so as to require 9–10 cc. of 0.01 *N* thiosulfate solution. The determina-

(2) The authors wish to express their indebtedness to Professor Herman Schlundt of the University of Missouri for placing this preparation at their disposal.

(3) Lind, *J. Ind. Eng. Chem.*, **7**, 406 (1915).

(4) Report of the International Radium-Standards Commission, *THIS JOURNAL*, **53**, 2437 (1931).

(5) For further details see Paneth and Vorwerk, Ref. 1.

tion of lead in a saturated solution of lead sulfate in water required 200-cc. samples, and in 0.0015 *N* sodium sulfate one-liter samples were taken. In all cases quantitative precipitation resulted upon addition of an excess of 0.1 molar potassium chromate in the presence of two to four drops of a 0.5% aluminum chloride solution. After digesting for several hours at 95°, a precipitate was obtained which could be filtered very easily. The extremely dilute lead solutions (saturated lead sulfate in sodium sulfate) required a digestion period of twenty to twenty-four hours. After digestion the cooled solution was filtered through a Gooch crucible, the precipitate washed and dissolved in 4 *N* hydrochloric acid, and titrated iodimetrically. The results were reproducible within 1 to 2%.

Determination of Adsorbed Sodium.—The sodium content of the very dilute solutions was determined according to the semi-micro volumetric method of I. M. Kolthoff and J. Lingane,⁶ yielding results reproducible within 1 to 2%.

Experimental Results

Solubility of Lead Sulfate in Water, Lead Nitrate and Sodium Sulfate Solutions.—Since the adsorption experiments were carried out at room temperature, the solubility of lead sulfate was determined under identical conditions. At 22 to 23° the solubilities of products I and II amounted to 2.8×10^{-4} *N* PbSO₄; at 26°, 3.0×10^{-4} *N*, at 28°, 3.1×10^{-4} , at 30°, 3.2×10^{-4} *N*.

In Table I the solubilities of lead sulfate in dilute lead nitrate and sodium sulfate solutions are recorded.

TABLE I

SOLUBILITY OF LEAD SULFATE IN LEAD NITRATE AND SODIUM SULFATE SOLUTIONS ^a						
Concn. lead nitrate <i>N</i> × 10 ⁴	Total Pb after satn. <i>N</i> × 10 ⁴	Soly. PbSO ₄ <i>N</i> × 10 ⁴	Temp., ^b °C.	Concn. sodium sulfate <i>N</i> × 10 ⁴	Soly. PbSO ₄ <i>N</i> × 10 ⁴	Temp., ^c °C.
5.01	6.49	1.48	29	5.05	1.45	26.5
7.50	8.69	1.19	29	7.45	1.15	26.5
10.00	10.88	0.88	29	10.11	1.00	27.5
15.00	15.76	.76	29	15.05	.80	26.5
25.00	25.47	.47	29			

^a Suspensions contained about 0.3 g. solid lead sulfate per liter. ^b Made at room temperature. ^c Made in thermostat.

Adsorption of Lead Nitrate and Sodium Sulfate by Lead Sulfate.—In the study of the adsorption of lead nitrate by lead sulfate, concentrated suspensions of the latter (product II) were shaken until equilibrium was reached, whereupon the lead concentration was determined in a manner already reported. From the figures in Table II it is evident that within the experimental error no adsorption of lead nitrate occurs.

In the determination of the adsorption of sodium sulfate the sodium content was determined before and after shaking.

Suspensions containing 10 g. of lead sulfate per 200 cc. were shaken with solutions 5×10^{-4} to 1.5×10^{-3} *N* in sodium sulfate. The same sodium concentration was found before and after shaking.

(6) Kolthoff and Lingane, *THIS JOURNAL*, **55**, 1871 (1933).

TABLE II
ADSORPTION OF LEAD NITRATE BY LEAD SULFATE^a

Lead nitrate $N \times 10^4$	Calcd. ^b concn. lead of satd. soln., $N \times 10^4$	Concn. lead found after shaking, $N \times 10^4$
5.05	6.53	6.60
7.57	8.76	8.72
10.11	10.99	11.22
15.17	15.93	15.78

^a Suspension of 8 g. lead sulfate per 200 cc. in thermostat at 29°. ^b These data are computed with the aid of the figures in Table I.

The Specific Surface of Lead Sulfate (I and II) in Suspensions in Water, Lead Nitrate and Sodium Sulfate.—In Table III the specific surface of lead sulfate (preparations I and II) suspended in water is given after various times of shaking.

TABLE III
SPECIFIC SURFACE OF LEAD SULFATE SUSPENDED IN WATER

Preparation I			Preparation II			
0.2093 g. PbSO ₄ per 33.90 cc. soln.			1.204 g. PbSO ₄ per 34.12 cc.			
Temp., 23° (Pb _{sol.} = $2.8 \times 10^{-4} N$)						
Time of shaking	% Th B adsorbed	Pb _{surf.} in 10^{-4} g. per 1 g. PbSO ₄	Time of shaking	Temp., °C.	% Th B adsorbed	Pb _{surf.} in 10^{-4} g. per 1 g. PbSO ₄
1.0 min.	7.3	3.7	1 min.	24.5	38.7	5.4
5.0 min.	9.2	4.8	5 min.	24.5	40.2	5.8
10.5 min.	11.9	6.4	15 min.	24.5	42.2	6.3
15.0 min.	13.1	7.1	30 min.	25.0	43.1	6.5
30.5 min.	14.8	8.2	1 hour	26.5	42.1	6.6
1 hour	15.1	8.4	2 hours	25	45.6	7.3
3 hours	17.6	10.1	6 hours	25	48.3	8.1
6 hours	18.1	10.4	12 hours	25	51.4	9.2
9 hours	18.6	10.8	24 hours	25.5	54.8	10.6
16 hours	21.1	12.6				
20 hours	22.3	13.5				

In Table IV the specific surface of both preparations of lead sulfate is recorded in the presence of an excess of lead nitrate. For reasons to be discussed later the values are given after one hour of shaking.

Table V gives the figures of the specific surface found after one hour of shaking in the presence of an excess of sodium sulfate.

It should be mentioned that in the various cases the thorium B was added after the suspension was in equilibrium with the particular electrolyte solution. If exactly weighed amounts of sodium sulfate were added to known volumes of suspensions of lead sulfate in water containing the thorium B, much more of the radioactive isotope was adsorbed than if the latter were added to the suspension in equilibrium with the sodium sulfate. In the former case there occurs a precipitation of lead and therefore of thorium B sulfate in addition to the kinetic exchange adsorption. The

TABLE IV

SPECIFIC SURFACE OF LEAD SULFATE IN THE PRESENCE OF AN EXCESS OF LEAD NITRATE AFTER ONE HOUR OF SHAKING

Preparation I			Preparation II					
0.933 g. PbSO ₄ per 37.5 cc. solution at 23°								
Pb(NO ₃) ₂ concn., $N \times 10^4$	% Th B adsorbed	Pb _{surf.} in 10^{-4} g. per 1 g. PbSO ₄	Pb(NO ₃) ₂ $N \times 10^4$	PbSO ₄ g.	Vol. soln., cc.	Temp., °C.	% Th B adsorbed	Pb _{surf.} in 10^{-4} g. per 1 g. PbSO ₄
5.00	20.3	7.0	0	1.204	34.12	26	42.1	6.6
7.50	16.2	7.0	5.01	0.989	34.15	25	20.5	5.9
10.00	13.4	7.1	7.50	1.066	34.14	23.7	19.1	6.6
50.00	(2.7)	(5.8)	10.03	1.031	34.14	23.8	15.6	6.8
75.00	(2.0)	(6.4)	15.04	1.142	34.13	23.6	11.6	6.3
			25.02	2.203	33.96	24.7	12.0	5.6

TABLE V

SPECIFIC SURFACE OF LEAD SULFATE IN THE PRESENCE OF AN EXCESS OF SODIUM SULFATE AFTER ONE HOUR OF SHAKING

Preparation I			Preparation II					
0.234 g. PbSO ₄ per 37.6 cc. solution at 23°								
Na ₂ SO ₄ $N \times 10^4$	% Th B adsorbed	Pb _{surf.} in 10^{-4} g. per 1 g. PbSO ₄	Na ₂ SO ₄ $N \times 10^4$	PbSO ₄ g.	Vol. soln., cc.	Temp., °C.	% Th B adsorbed	Pb _{surf.} in 10^{-4} g. per 1 g. PbSO ₄
5.0	25.1	7.6	0	1.204	34.12	26	42.1	6.6
7.5	24.8	7.0	5.02	0.362	33.90	21.5	33.3	6.6
10.0	34.3	7.3	7.52	.330	34.11	22.3	35.0	5.9
25.0	43.2	(7.0)	10.02	.302	34.11	25.4	28.4	4.4 ^b
50.0	48.9	^a	15.04	.294	34.11	26.5	32.2	4.6 ^b
75.0	55.0	^a						
100	57.3	^a						

^a The specific surface has not been calculated in suspensions containing more than 0.0025 N sodium sulfate, as the solubility of lead sulfate in those solutions is too small to give reliable data according to the analytical procedure used. Since the figures in the table indicate that the specific surface is constant in the presence of an excess of sodium sulfate, the radioactive method might be applied to the determination of the solubility of lead sulfate in fairly concentrated sulfate solutions.

^b In these two cases an agglomeration of the lead sulfate particles was noticeable with the naked eye. The particles became curdy and showed a tendency to float on the surface of the solution. This tendency of the fine crystals to combine in larger groupings is responsible for the apparent decrease of the specific surface of the solid in these two suspensions.

data thus obtained cannot be used in the calculation of the specific surface of lead sulfate. However, in the experiments reported precipitation was avoided by dissolving the thorium B in a lead sulfate solution having a concentration which would prevent such loss of the radioactive substance.

Microscopic Measurements.—The dimensions of some fifty crystals of the two preparations of lead sulfate were measured microscopically. The average of all readings is reported in the following:

Length in μ	11.2 (prep. I); 7.3 (prep. II)
Width in μ	2.11 (prep. I); 1.19 (prep. II)
Specific surface in d.M. ² p. 1 g.	33.4 (prep. I); 58.2 (prep. II)

Discussion of the Results

1. The solubility determinations described in the experimental part are accurate within 1 to 2%. The figures recorded for the saturated solutions in water are in good agreement with the average values given in the literature.⁷ Paneth and Vorwerk¹ used six different preparations of lead sulfate and determined the solubility (only in water) by evaporating 50 to 100 cc. to dryness and weighing the residue. Their values varied between 7.7 and 9.2×10^{-4} g. of lead per 25 cc. of solution, all figures being higher than those reported in the literature and those given in this paper. There is a possibility that the preparations used by P. and V. were not quite pure but contained a slight amount of adsorbed lead salt.

In the radioactive work, suspensions were used containing amounts of solid much larger than usually are taken in solubility determinations. In the present work it was shown that prolonged shaking of the suspensions with intermittent washings was necessary to find a constant solubility, especially so when large amounts of solid were present.

2. Paneth and Vorwerk¹ determined the adsorption of thorium B over a period of shaking for thirty-seven minutes and concluded that kinetic exchange equilibrium was established after shaking for three minutes. In the work reported in this paper (compare Table III) the change of the percentage adsorption per minute was 0.6 after one, 0.48 after five, 0.24 after fifteen, 0.12 after thirty, 0.01 after sixty and 0.003 after three hundred and sixty minutes. From this it was inferred that the kinetic exchange equilibrium was established after about one hour of shaking. In our work it is noticeable that even after twenty-four hours of shaking no adsorption equilibrium is established, the adsorption of thorium B being increased with longer shaking. L. Imre⁸ attributes this increase to an internal recrystallization of the lead sulfate, lead and sulfate ions leaving the surface at a certain spot and depositing on other active spots.

In the present work the lead sulfate was aged by shaking over a period of a few months; therefore it could be expected that internal equilibrium within the crystal had been established. For this reason Imre's interpretation does not seem to be warranted for this particular case. Paneth and Vorwerk ascribe the time effect upon the adsorption either to a mechanical breaking up of the crystal aggregates at the high speeds of shaking or to a slow diffusion into and adsorption at the walls of capillaries and cracks present in every real crystal. In the present work it was found that the magnitude of the "secondary adsorption" did not decrease after prolonged

(7) Considering the agreement between our figures and those of some previous authors, it seems that the data reported in the "International Critical Tables" need revision.

(8) Imre, *Z. physik. Chem.*, **A153**, 127, 261 (1931); *Z. Elektrochem.*, **38**, 535 (1932).

aging of the crystals. Therefore there is much reason to believe that imperfections in the crystals are not entirely responsible for the secondary adsorption, but that with time of shaking molecules of lead sulfate under the surface layer participate in the exchange adsorption. Only with infinite time of shaking can one expect to have the same ratio of thorium B and lead in the crystals as in the supernatant solution. It may be mentioned here that various experiments have been carried out with air dry lead sulfate, obtained by filtering the standard suspension and washing with a little alcohol. This treatment left the specific surface unchanged.

3. In agreement with Paneth and Vorwerk¹ it was found that the specific surface in lead nitrate solutions was the same as in suspensions in water. Paneth and Vorwerk¹ derived an equation by means of which they tried to calculate the amount of lead ions adsorbed on the surface of lead sulfate under various conditions. They found, for example, that a certain preparation of lead sulfate, having a specific surface of 1.29 mg. lead, adsorbed per gram of precipitate 0.5 mg. of lead ions, suspended in water, this figure increasing to 1.2 mg. in a suspension containing 5×10^{-3} molar lead as nitrate in solution. These figures would indicate that in the suspension of the salt in water about 40% of the surface was covered by adsorbed lead ions, whereas the surface was approximately covered with a monatomic layer of lead ions in a solution containing 0.005 molar lead nitrate. However, the equation used by P. and V. is incorrect and consequently the conclusions inferred from it are not justified. Fundamentally, the following equation is sound:⁹

$$\frac{\text{Th } B_{\text{surf.}}}{\text{Th } B_{\text{sol.}}} = \frac{\text{Pb}_{\text{surf.}}}{\text{Pb}_{\text{sol.}}} = \frac{\text{Total Pb}_{\text{surf.}}}{\text{Total Pb}_{\text{sol.}}} = \frac{\text{Pb}_{\text{surf.}} + \text{Th } B_{\text{surf.}}}{\text{Pb}_{\text{sol.}} + \text{Th } B_{\text{sol.}} + \text{Th } B_{\text{surf.}}}$$

Th $B_{\text{surf.}}$ is the concentration of the radioactive lead, Pb $_{\text{surf.}}$ that of the inactive lead in the surface; total Pb $_{\text{surf.}}$ denotes the sum of the two. Since in all cases Th $B_{\text{surf.}}$ and Th $B_{\text{sol.}}$ are at least 10^5 to 10^8 times smaller than the corresponding concentrations of the inactive lead, the above equation may be written as well in the form

$$\frac{\text{Th } B_{\text{surf.}}}{\text{Th } B_{\text{sol.}}} = \frac{\text{Total Pb}_{\text{surf.}}}{\text{Total Pb}_{\text{sol.}}}$$

Total Pb $_{\text{sol.}}$ represents the concentration of the lead analytically determined and Total Pb $_{\text{surf.}}$ the specific surface calculated in the experimental part. An adsorption of lead ions from lead nitrate solutions would result in an increase of the concentration of lead at the surface, and therefore also of the specific surface. From the fact that the specific surface of lead sulfate suspended in lead nitrate solutions is found to be the same as that in water, it may be concluded that no measurable adsorption of lead ions from lead nitrate solutions takes place. Considering the experimental error involved in the radioactive method it is safer to state that under the

(9) See F. Paneth, *Physik. Z.*, **15**, 924 (1914).

conditions mentioned the adsorption of lead ions amounts to less than 4 to 5% of the specific surface.

In the experimental part it has likewise been shown that the specific surface remained unchanged in the presence of an excess of sodium sulfate in the solution. Thus from the constancy of the specific surface it is concluded that under the experimental conditions there is no measurable adsorption by lead sulfate of either lead ions from lead nitrate solutions or of sulfate from sodium sulfate solutions. It is quite possible and it is anticipated that such an adsorption will be found if preparations of lead sulfate with a much larger specific surface are used.

4. The above conclusion is substantiated by the adsorption studies made with the aid of chemical methods. The suspensions used in these experiments contained the same amount of solid as those of P. and V. in their radioactive measurements, whereas the average size of the crystals was of the same order as that used by the above mentioned authors. An adsorption amounting to a covering of the surface of 10% by adsorbed ions would have been detected easily by the chemical method.

5. The specific surface of preparation I after one hour was found to be equal to 8.37×10^{-4} g. of lead per 1 g. of lead sulfate. This means that there are $\frac{8.37 \times 10^{-4}}{207} \times 6.06 \times 10^{23} = 24.5 \times 10^{17}$ ions of lead in the surface of 1 g. lead sulfate. Assuming the crystals to be cubic and having a density of 6.23, it is calculated that there are $\sqrt[3]{(6.23/303.3) \times 6.06 \times 10^{23}} = 2.32 \times 10^7$ molecules of lead sulfate per 1 cm., and the size of 1 molecule equals 4.32×10^{-8} cm.

From this value we find the surface per molecule equal to $(4.32 \times 10^{-8})^2$ sq. cm., and the specific surface of preparation I, $18.6 \times 10^{-16} \times 24.5 \times 10^{17}$ sq. cm. = 45.5 d.M.². The microscopic measurements yielded a specific surface of 33.4 d.M.². Considering the great uncertainty in the microscopic measurements the agreement is very satisfactory.

The number of particles n per gram of lead sulfate (preparation I) is equal to $n = \text{specific surface in sq. cm.}/6x^2 = 4550/6x^2$, in which x is the size of a particle, the latter assumed to be cubic. Since $x^3 \times n = 1/6.23$, it is found that $x = 2.12 \times 10^{-4}$ cm., and $n = 1.69 \times 10^{10}$ particles per gram.

From the above figures it is derived that the surface occupied by the edges equals

$$2 \times 12 \times 2.12 \times 10^{-4} \times 2.32 \times 10^7 \times 1.69 \times 10^{10} \times 18.6 \times 10^{16} = 3.72 \text{ sq. cm. per 1 g. of lead sulfate.}$$

The total surface of 1 g. was found to be 4550 sq. cm. Therefore it is quite possible that lead nitrate and sodium sulfate are adsorbed on the edges of the lead sulfate. If all of the molecules of lead sulfate in the edges had been completely covered by adsorbed lead or sulfate ions, the adsorption

would amount to less than 0.1% of the total surface, which is beyond detection by the experimental methods used.¹⁰

In a similar way to that for preparation I a specific surface of 35.8 d.M.² has been calculated per 1 g. of preparation II, whereas the microscopic measurements yielded an average of 58 d.M.². Again the surface occupied by the edges is negligibly small as compared with the total surface.

The authors wish to acknowledge their gratitude to Professor S. C. Lind for technical advice given with regard to the radioactive measurements and for his interest in the investigation.

Summary

1. The solubilities of lead sulfate in water, dilute lead nitrate, and dilute sodium sulfate solutions have been determined.

2. The specific surface of lead sulfate is the same in suspensions in water, dilute lead nitrate, and sodium sulfate solutions. The constancy of the specific surface indicates that the adsorption of lead and sulfate ions at the surface of lead sulfate is negligibly small. This result has been substantiated by adsorption measurements according to chemical methods. If any adsorption takes place, it must be limited to the corners and edges.

(10) In a private communication Professor H. R. Kruyt (Utrecht) informed the senior author that he had arrived at the conclusion that silver ions are adsorbed only at the corners and edges of silver iodide.

MINNEAPOLIS, MINNESOTA

RECEIVED FEBRUARY 8, 1933

PUBLISHED JULY 6, 1933

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Adsorption of Ponceau 4R (New Coccine) and Methylene Blue by Lead Sulfate and the Influence of Adsorbed Ponceau on the Speed of Kinetic Exchange

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

F. Paneth and Vorwerk¹ have determined the adsorption of Ponceau 2R by lead sulfate and claim that the dye forms a monomolecular layer at the saturated surface of the solid. The work of these authors has been extended in this paper to the measurement of the adsorption of Ponceau 4R by lead sulfate in the presence of an excess of lead nitrate and of sodium sulfate; in addition, the adsorption of methylene blue has been determined under similar conditions. During the course of the work indications were obtained that adsorbed Ponceau inhibits the speed of kinetic exchange at the interface of lead sulfate and water. This has been substantiated by the measurement of the specific surface by means of the radioactive method in the presence of adsorbed dye at the surface of lead sulfate.

(1) Paneth and Vorwerk, *Z. physik. Chem.*, **101**, 480 (1922); see also Paneth and Thimann, *Ber.*, **57**, 1215 (1924).