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.

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[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.

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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 Vorwerk[1] 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.

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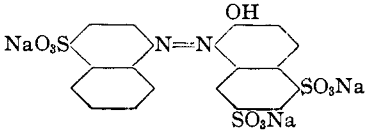
[1] Paneth and Vorwerk, *Z. physik. Chem.*, **101**, 480 (1922); see also Paneth and Thimann, *Ber.*, **57**, 1215 (1924).

The results are of interest in regard to the problem of crystal growth in the presence of adsorbed material.

Materials Used.—The preparations I and II of lead sulfate were the same as described in a previous paper.[2]

Methylene Blue.—U. S. P. product.

Ponceau 4R.—The product was different from that of Paneth and Vorwerk. Ponceau 4R has the constitution[3]



Mol. Weight = 604.3

A Kahlbaum product was thrice recrystallized from water and dried at 95–100°. The sodium content was determined according to Barber and Kolthoff's[4] method and was found to be equal to 11.22% (calcd. 11.42%).

Experimental Methods

Paraffined bottles stoppered with paraffined corks have been used in all experiments. The solutions were saturated with lead sulfate before any adsorption experiment was made. Separation of the solid lead sulfate from the solutions was effected by centrifuging, thus avoiding any losses by adsorption during filtration. The concentrations of Ponceau 4R and methylene blue were determined colorimetrically by comparing with dye solutions of approximately the same strength. After some practice the colorimetric method yields results reproducible within 2%. Blank experiments showed that small amounts of Ponceau as used in the adsorption experiments had no influence upon the radioactive measurements. The speed of shaking was the same as in the earlier experiments.

Experimental Results

The Adsorption of Ponceau 4R by Lead Sulfate.—Table I shows that adsorption equilibrium is reached after a short time of shaking of the dye with the suspensions in water, lead nitrate and sodium sulfate. The amount of dye adsorbed is expressed in mg. of the Ponceau radical and not of the sodium salt, since the sodium is not adsorbed, as will be shown later. Similar experiments have been made with suspensions of preparation II, yielding the same results. The data show that adsorption equilibrium is established after about thirty minutes of shaking. In the following work the suspensions were shaken for one hour, unless stated otherwise.

Table II shows the change in the adsorption of Ponceau 4R with decreasing concentration of the dye in the solution. The data recorded are the average of three independent sets of measurements which gave results agreeing within 2%.

Table III reveals the influence of an excess of lead nitrate or of sodium sulfate upon the adsorption of Ponceau by preparation II.

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(2) Kolthoff and Rosenblum, THIS JOURNAL, **55**, 2656 (1933).

(3) Schulz, "Farbstofftabellen," 6th Ed., No. 165, 1923.

(4) Barber and Kolthoff, THIS JOURNAL, **50**, 1625 (1928).

TABLE I

ADSORPTION OF PONCEAU 4R BY LEAD SULFATE, 0.878 G. $PbSO_4$ (PREP. I) PER SAMPLE

Medium	Concn. of dye in mg. per liter Before ads.	After ads.	Vol. soln., cc.	Time of shaking	Mg. Ponceau radical adsorbed per 1 g. $PbSO_4$
Water	55.1	46.7	34.13	5 min.	0.29
Water	55.1	46.6	34.13	15 min.	.29
Water	55.1	46.1	34.13	35 min.	.31
Water	55.2	45.9	34.13	1 hour	.32
Water	55.0	46.3	34.13	7 hours	.30
Water	55.2	46.1	34.13	41 hours	.31
10^{-3} N $Pb(NO_3)_2$	49.5	39.3	37.93	5 min.	.39
10^{-3} N $Pb(NO_3)_2$	49.6	37.6	37.93	15 min.	.46
10^{-3} N $Pb(NO_3)_2$	49.6	38.0	37.93	35 min.	.44
10^{-3} N $Pb(NO_3)_2$	49.5	36.[illegible]	37.93	1 hour	.50
10^{-3} N $Pb(NO_3)_2$	49.6	36.8	37.93	7 hours	.49
10^{-3} N $Pb(NO_3)_2$	49.5	36.0	37.93	41 hours	.51
10^{-3} N Na_2SO_4	49.6	46.2	37.95	15 min.	.13
10^{-3} N Na_2SO_4	49.5	46.3	37.95	1 hour	.12
10^{-3} N Na_2SO_4	49.6	45.8	37.95	6 hours	.11
10^{-3} N Na_2SO_4	49.5	46.3	37.95	24 hours	.11
10^{-2} N Na_2SO_4	49.5	49.0	37.97	1 hour	(.02)
10^{-2} N Na_2SO_4	49.6	48.8	37.97	6 hours	(.03)

TABLE II

ADSORPTION OF PONCEAU 4R AS A FUNCTION OF THE DYE CONCENTRATION

1.204 g. $PbSO_4$ (preparation II) + 34.21 cc. dye solution in saturated lead sulfate in water. Time of shaking, 1 hour.

Concn. of dye in mg. per liter Before ads.	After ads.	Dye ads., %	Mg. of Ponceau radical ads. per 1 g. $PbSO_4$
322	312	3.2	0.27
161	150	6.9	.28
80.5	70.8	11.6	.24
40.2	34.2	15.2	.16

TABLE III

ADSORPTION OF PONCEAU 4R IN PRESENCE OF AN EXCESS OF LEAD AND SULFATE PPT. II; SHAKEN FOR 1 HOUR

Medium	$PbSO_4$ g.	Suspension shaken, cc.	Concn. of dye in mg. per liter Before ads.	After ads.	Mg. Ponceau radical ads. per 1 g. $PbSO_4$
Water	1.204	34.21	322	312	0.27
5.01×10^{-4} N $Pb(NO_3)_2$	0.989	34.24	322	280	1.3
5.01×10^{-4} N $Pb(NO_3)_2$	.989	34.24	161	118	1.3
7.50×10^{-4} N $Pb(NO_3)_2$	1.066	34.23	322	255	1.9
7.50×10^{-4} N $Pb(NO_3)_2$	1.066	34.23	161	114	1.3
1.00×10^{-3} N Na_2SO_4	0.299	34.20	40.3	39.5	0.1
1.00×10^{-3} N Na_2SO_4	.286	34.20	32.3	31.2	.1

Several experiments have been made in which the sodium concentration of the dye solution was determined before and after adsorption.[5] Neither

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[5] The authors express their gratitude to J. Lingane for performing these sodium determinations.

in the suspensions in water nor in the presence of an excess of lead nitrate or sodium sulfate was there an adsorption of sodium. In order to be quite sure that the results were correct, experiments were made with large amounts of lead sulfate. Thus 45.5 g. of lead sulfate (Ppt. II) was shaken with 92.6 cc. of a dye solution containing 119.3 mg. of Ponceau salt or 13.6 mg. of sodium per liter. After adsorption equilibrium was established, the concentration of the dye amounted to 39.7 mg. per liter corresponding to an adsorption of 67%. The results of the sodium analyses showed a sodium content of 13.6 mg. per liter before and of 13.8 mg. per liter after adsorption, thus showing that only the Ponceau ion is removed by adsorption.

Adsorption of Methylene Blue by Lead Sulfate.—W. D. Bancroft and C. E. Barnett[6] determined the adsorption of methylene blue as a function of the *P*H of the medium. They added varying amounts of sodium hydroxide to the lead sulfate suspensions and measured the *P*H and the adsorption of the dye. Their results, however, do not indicate that the *P*H actually has an influence upon the adsorption, since the addition of alkali hydroxide to the lead sulfate suspensions results in a change of the solid body (basic salt formation).

The results in Table IV show that the adsorption of methylene blue is small as compared with that of Ponceau 4R. Such a result could be expected, since the solubility of the lead salt of Ponceau is much smaller than that of the sulfate of methylene blue. The experiments have been performed with both preparations of lead sulfate. For the sake of brevity only one set of data will be presented. The effect of an excess of the lattice ion in the solution was found to be the same for both preparations.

TABLE IV

ADSORPTION OF METHYLENE BLUE BY LEAD SULFATE (PPT. I)

0.878 g. $PbSO_4$ per sample

Medium	Concn. of dye in mg. per liter Before ads.	After ads.	Solution, cc.	Time of shaking	Mg. methylene blue adsorbed per 1 g. of $PbSO_4$
Water	53.1	51.4	34.26	15 min.	0.07
Water	53.1	51.5	34.26	70 min.	.06
Water	53.2	51.9	34.26	6 hours	.06
10^{-3} *N* $Pb(NO_3)_2$	47.8	47.6	38.05	15 min.	.01
10^{-3} *N* $Pb(NO_3)_2$	47.8	47.5	38.05	1 hour	.01
10^{-3} *N* $Pb(NO_3)_2$	47.9	47.3	38.05	6 hours	.02
10^{-3} *N* Na_2SO_4	47.8	45.8	38.05	15 min.	.09
10^{-3} *N* Na_2SO_4	47.8	45.4	38.05	70 min.	.10
10^{-3} *N* Na_2SO_4	47.8	46.1	38.05	6 hours	.08

Influence of Adsorbed Ponceau 4R upon the Speed of Kinetic Exchange.—The following experiments have been made in two ways. (a) The lead sulfate suspension was shaken for one hour with the Ponceau solution, then thorium B solution of known activity was added and the

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[6] Bancroft and Barnett, "Colloid Symposium Annual," **6**, 73 (1928).

mixture shaken for another hour. After centrifuging the activity of the supernatant liquid was determined as described in a previous paper.[2] (b) The suspension was shaken first for one hour with Th B, then a known amount of Ponceau added. After shaking for another hour, the radioactivity of the centrifugate was determined. The dye was added in the solid form and weighed out on a micro balance.

In the following tables the specific surface found in the presence of the

TABLE V

LEAD SULFATE SHAKEN FOR ONE HOUR WITH PONCEAU; THEN Th B ADDED AND SHAKEN FOR ANOTHER HOUR

Medium	Concn. of dye, mg. per liter	$PbSO_4$, g.	Soln., cc.	Th B adsorbed, %	Sp. surface $PbSO_4$ Mg. per 1 g.	Sp. surface in absence of dye after 1 hour of shaking
Water	162	1.204	34.12	37.2	0.49	0.66
				35.8		
5×10^{-4} *N* $Pb(NO_3)_2$	161	0.989	34.15	25.0	.75	.59
				24.4		
7.50×10^{-4} *N* $Pb(NO_3)_2$	164	1.066	34.14	27.9	1.11	.60
				28.7		
5.02×10^{-4} *N* Na_2SO_4	161	0.362	33.90	27.0	0.53	.66
				28.1		
7.5×10^{-4} *N* Na_2SO_4	155	.330	34.11	31.4	.53	.60
				28.6		
1.00×10^{-3} *N* Na_2SO_4	73.4	.302	34.11	24.6	.35[b]	(.43)[b]
				23.5		
1.5×10^{-3} *N* Na_2SO_4	(138)[a]	.294	34.11	24.7	.335[b]	(.41)[b]
	(61.6)			26.3		

[a] Different quantities of dye were added to show that the procedure adopted did not affect the measurement. [b] For interpretation of low values see Ref. 2.

TABLE VI

LEAD SULFATE SHAKEN FOR ONE HOUR WITH THORIUM B, THEN PONCEAU ADDED AND SHAKEN FOR ANOTHER HOUR

Medium	Concn. of dye mg. per liter	$PbSO_4$, g.	Soln., cc.	Th B. adsorbed, %	Sp. surface $PbSO_4$ mg. per 1 g.	Sp. surface in absence of dye after 1 hour of shaking
Water	170	1.204	34.12	53.4	0.97	0.72
				50.3		
5.01×10^{-3} *N* $Pb(NO_3)_2$	161	0.989	34.15	30.2	1.00	.72
				30.7		
7.5×10^{-4} *N* $Pb(NO_3)_2$	164	1.066	34.14	41.6	2.23	.80
				46.7		
5.02×10^{-4} *N* Na_2SO_4	160	0.362	33.90	32.8	0.63	.73
				30.7		
7.5×10^{-4} *N* Na_2SO_4	154	.330	34.14	36.0	.69	.72
				36.1		
1.00×10^{-3} *N* Na_2SO_4	158	.302	34.14	27.5	(.42)	(.46)
	79.2			27.7		
1.5×10^{-3} *N* Na_2SO_4	161	.294	34.14	31.3	(.45)	(.41)
	64.5			31.9		

dye is reported. Since the adsorption of thorium B increases with the time of shaking, figures of the specific surface found after one and two hours of shaking in the absence of the dye have been added. Preparation II of lead sulfate has been used in all cases.

Discussion of Results

1. Adsorbed Ponceau 4R is more strongly adsorbed by lead sulfate than methylene blue. It appears from Table II that the surface of precipitate II is saturated with Ponceau at a dye concentration of about 100 mg. per liter. At this concentration there are 0.27 mg. of Ponceau ions adsorbed per gram of lead sulfate, corresponding to 3.06×10^{17} ions of dye per 1 g. of solid. In a previous paper[2] it has been computed that this preparation of lead sulfate contains 19.3×10^{17} molecules of lead sulfate in the surface per 1 gram. Therefore in the saturated solution there is approximately one Ponceau ion adsorbed per 6 molecules of lead sulfate in the surface. A corresponding calculation for precipitate I yields a ratio of 1 to 7. The agreement is satisfactory considering that the adsorption by precipitate I was determined at a dye concentration slightly below that at which the surface is saturated. The results indicate that the adsorption of Ponceau by lead sulfate is not limited to the corners and edges, but that it takes place over the entire surface.

Paneth and Vorwerk[1] found that in the saturated state 1 molecule of Ponceau 2R was adsorbed per 11 molecules of lead sulfate in the surface.

It is worth while mentioning that the time–adsorption curve of Ponceau red and of methylene blue is entirely different from that of thorium B. The adsorption of the latter increases even after hours of shaking, whereas in the adsorption of the dyes a constant value is obtained after less than thirty minutes. This might be explained by the fact that the dye ions are too large to allow a diffusion into the capillaries and cracks of the crystals. However, it seems more plausible to interpret the effect with the assumption that the adsorbed Ponceau inhibits the speed of kinetic exchange at the surface of the lead sulfate as will be shown below.

2. The adsorption of Ponceau increases in the presence of an excess of lead nitrate and decreases with excess of sulfate in the solution. This result could be expected and is in agreement with experiments of K. Fajans and T. Erdy Gruz,[7] who found that the adsorption of erythrosin at the surface of silver bromide decreases in the presence of an excess of bromide and increases with increasing silver ion concentration. The opposite effect was found in the adsorption of the basic dye phenosafranin by silver bromide.

3. It is tacitly assumed in the literature that the adsorption of a foreign electrolyte by an ionic lattice results in an equivalent adsorption of the

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(7) Fajans and Gruz, *Z. physik. Chem.*, **A158**, 97 (1931).

foreign cation and anion. This has been shown not to be the case in the adsorption of Ponceau 4R by lead sulfate, the Ponceau ion being adsorbed whereas the sodium remains quantitatively in the solution. This result cannot be attributed to a hydrolytic adsorption of the free acid of the dye, as was shown by the following experiments.

The P_{H} of a dye solution shaken with much lead sulfate was slightly less after adsorption than it was before (P_{H} 5.8 before, 5.6 after adsorption). A hydrolytic adsorption of the free acid of the dye would have resulted in a more alkaline reaction after the adsorption. In addition it was found that the adsorption of Ponceau from 0.001 N nitric acid was the same as in the absence of acid.

The results therefore clearly indicate that we are dealing here with a case of exchange adsorption, the adsorbed Ponceau ions replacing sulfate ions at the surface of the lattice. This means then that on shaking lead sulfate with Ponceau, sulfate ions leave the surface, thus giving an excess of these ions in the solution. This results in a decrease of the lead-ion concentration in the solution. Experimentally it was shown that the lead concentration of a saturated lead sulfate solution in dilute Ponceau in equilibrium with much lead sulfate was smaller than that in water. It should be mentioned here that recently much more convincing experiments have been carried out in this Laboratory with other precipitates, showing that the solubility of an ionic precipitate in an electrolyte solution depends upon the amount of solid present. The conclusive evidence will be published soon by the senior author with Dr. E. B. Sandell.

The exchange adsorption described in this paper corresponds to a surface reaction:

$$\underset{\text{surface}}{3\mathrm{Pb}^{++}\mathrm{SO}_4^{=}} + \underset{\text{solution}}{2\mathrm{Ponc}^{\equiv}} \longrightarrow \underset{\text{surface}}{2\mathrm{Pb}_3^{++}\mathrm{Ponc}_2^{\equiv}} + \underset{\text{solution}}{3\mathrm{SO}_4^{=}}$$

This reaction is limited only to the surface, the solid lead Ponceau salt is not in equilibrium with the system as its solubility product is not exceeded. This is clearly indicated by the fact (Table II) that the final concentration of the dye in the solution is not constant at the state of equilibrium, but decreases with decreasing initial concentration of Ponceau.

The interpretation then of the effect of an excess of sulfate upon the adsorption of Ponceau is different from the classical one. In the previous paper it has been shown that no sulfate is adsorbed by lead sulfate from dilute sodium sulfate solutions. The decrease of the adsorption of Ponceau in the presence of sodium sulfate is explained by the fact that the exchange is made less favorable by the excess of sulfate in the solution. Quite generally there is a competition between the sulfate and Ponceau ions to be fixed at the surface of lead sulfate. An increase of the sulfate concentration of the solution hinders the exchange, a decrease (excess of lead) favors it.

4. The strong affinity between Ponceau ions and lead is explained by the

slight solubility of the lead Ponceau salt. Approximate determinations showed that the solubility product $[Pb^{++++}]^3[Ponc^{\equiv}]^2 \gg 2 \times 10^{-19}$. No claim is made of great accuracy. The figure shows definitely that according to the mass action law no precipitation of lead Ponceau can occur by shaking an aqueous suspension of lead sulfate with the dilute sodium solution of the dye.

However, it is quite possible that the large increase of the dye adsorption in the presence of an excess of lead nitrate in the solution is to be attributed partly to a slight precipitation of the lead salt of the dye (Tables III, V and VI).

5. If lead sulfate is shaken first with Ponceau and then with thorium B, a specific surface is found which is much smaller than when the order of addition is reversed (Tables V and VI). In the latter case the kinetic exchange equilibrium between the thorium B and lead sulfate is established before the dye is added. The addition of Ponceau thereafter prevents a further adsorption of thorium B at the interior of the crystals. However, it should be realized that the addition of Ponceau gives an exchange with sulfate ions in the surface, resulting in a slight precipitation of lead and thorium B sulfate from the solution. This explains why the specific surface found in the first experiment reported in Table VI is larger than in the absence of the dye after the same time of shaking. The increase of the specific surface in the presence of an excess of lead (Table VI) is explained by an adsorption of the lead salt of Ponceau or a slight precipitation of the latter (Comp. sub. 4).

If the lead sulfate is shaken first with Ponceau and then thorium B added, the specific surface found is smaller than in the absence of the dye (Table V; for the interpretation of the opposite effect found in the presence of an excess of lead, the reader is referred to the above). These experiments show definitely that adsorbed Ponceau inhibits the speed of kinetic exchange at the interface water–lead sulfate. This conclusion was substantiated by the following experiments.

Lead sulfate was covered with Ponceau by one hour of shaking with the dye. Thorium B was added to the suspension and the specific surface determined after five minutes of shaking. A value of 0.36 mg. was found (preparation II). After the same time of shaking with uncoated lead sulfate, a specific surface of 0.58 mg. was found. Corresponding experiments after one hour of shaking with thorium B yielded specific surfaces of 0.49 and 0.66 mg. (Table V). Thus the specific surface of the coated precipitate after five minutes of shaking with thorium B was 62% of that found for the pure solid, whereas after one hour of shaking it amounted to 74%. The figures indicate clearly that adsorbed Ponceau hinders the establishment of the kinetic equilibrium.

On the other hand, the following experiments show that adsorbed Ponceau does not inhibit the speed of exchange between sulfate and dye ions in a marked way when there is an excess of the former in the solution. Lead sulfate was shaken with a 0.00075 *N* sodium sulfate for two days; then dye added corresponding to a concentration of 15 mg. of dye per liter of suspension. After two days of continued shaking, the amount of dye adsorbed corresponded to 23%. The adsorption of the dye in the absence of an excess of sulfate amounted to 37% after three hours of shaking. To such a suspension sodium sulfate was added making the solution 0.00075 *N*. After continued shaking for fifteen minutes, the amount of dye adsorbed had decreased to 25%, showing no further decrease after two days. From the latter experiments it may also be inferred that the exchange between sulfate and dye ions at the surface of lead sulfate is a reversible process.

Summary

1. A suspension of lead sulfate saturated with Ponceau 4R contains approximately one Ponceau ion adsorbed per six molecules of lead sulfate at the surface.

2. On shaking the sodium salt of Ponceau with lead sulfate, an exchange adsorption takes place. The sulfate ions in the surface are partly replaced by an equivalent amount of Ponceau ions, thus yielding a solution containing sulfate in excess of lead. No adsorption of sodium is found. The influence of an excess of lead and sulfate in the solution is interpreted on the basis of this exchange adsorption.

3. The adsorption of Ponceau 4R by lead sulfate is much greater than that of methylene blue.

4. Adsorbed Ponceau ions inhibit the speed of kinetic exchange of thorium B at the interface lead sulfate–water.

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