

The subject of our next work will be the results of biochemical investigations conducted on luminescent extracts for the purpose of ascertaining the nature of the enzymatic reaction which is responsible for the luminescence.

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Riassunto

Alcuni di noi recentemente hanno messo in evidenza un'emissione di luce di debole intensità nello spettro visibile, da parte di semi in germinazione. E argomento del presente lavoro discutere alcune accurate misure di intensità luminosa condotte su semi germinanti e su loro estratti acquosi in varie condizioni di età della plantule da 1 a 20 giorni. Viene anche studiata la dipendenza dell'emissione luminosa dal pH della soluzione e viene indicata la distribuzione spettrale della luce emessa.

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Area and Degree of Occupation of the Surface of Precipitates of Barium Sulphate

Precipitates of BaSO₄ were prepared by pouring 2 l of a 0.1 N hot solution of H₂SO₄ into 2 l of a 0.1 N hot solution of BaCl₂, under constant stirring; stirring was continued for 1 h; then the precipitate of BaSO₄ was separated from the solution, washed with hot and cold twice distilled water, washed with ethanol, and stocked under ethanol.

Photographs of the precipitate were taken with the optical microscope (1200 ×) and the electron microscope (3000 × and 10,000 ×); the surface average particle diameter was 2.7 μ, corresponding to a specific surface area of 0.51 m²/g. This value agrees with the value given by KOLTHOFF¹ (about 1 m²/g), but not with that given by DE BROUCKÈRE² (about 80 m²/g).

We then studied the exchange of Ba*-ions (i.e. radioactive Ba-ions) between a saturated solution of Ba*SO₄ and precipitate of BaSO₄. The isotope used was Ba* 131, $\tau_{1/2}$ = 12 days, emitter of γ -rays, no β 's. When AMERSHAM delivered the radioactive material, they warned us that the activity was 600 times higher than expected; this must be attributed to an error in the assumed neutron cross-section of Ba 130, a point which now is being investigated in AMERSHAM; for us it was a lucky circumstance, since it enabled us to solve our problem easily.

We shook 100 cm³ of saturated solution of Ba*SO₄ at 16°C, hence containing 0.000215 g of BaSO₄ per 100 cm³, or 5.54×10^{17} Ba-ions, with 100 mg precipitate of BaSO₄, and measured the γ -radio activity of 4 cm³ of the

solution after 0, 0.5, 1, 2, 3, 5, 10, 20, and 35 min. The results are given in Figure 1; a correction for background has been applied; we attribute the slow decrease at higher time periods to an exchange with the inward part of the lattice of BaSO₄; we therefore extrapolate this part of the curve back to $t = 0$ in order to obtain the true equilibrium between surface and precipitate; in this way we find: For the original solution at $t = 0$: 2829 counts/min. For the solution when equilibrium is reached, correction applied for exchange with the inward part of the lattice: 1919 counts/min.

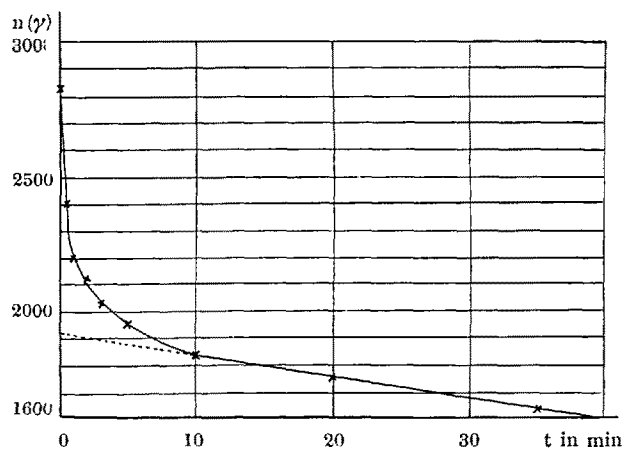
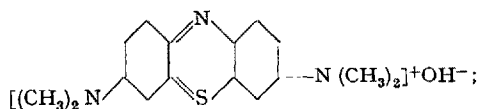


Fig. 1.— Number of γ -counts/min of 4 cm³ of the solution as a function of the time of shaking.

From this we calculate that the surface of BaSO₄ contains 2.63×10^{18} Ba-ions/g. With 19.6×10^{-16} cm² for the surface area/molecule of BaSO₄, we find a surface area of 0.515 m²/g BaSO₄.

We then studied the adsorption of crystal violet (hexamethyl para rosaniline); methylene blue



and picric acid by our precipitates of BaSO₄; the adsorption was measured by measuring (with a Cambridge Unicam SP 500 Spectrophotometer) the difference in extinction between the original solution and the solution in which the adsorption equilibrium with a precipitate of BaSO₄ had established itself; measurements with crystal violet showed that equilibrium was reached after 30 min shaking; in all our experiments we shook solution and precipitate together for 1 h.

We first studied the extinction as a function of wave length for the 3 substances, and found extinction maxima for

picric acid at	$\lambda = 3550 \text{ \AA}$
methylene blue at	$\lambda = 6630 \text{ \AA}$ (and $\lambda = 6125 \text{ \AA}$)
crystal violet at	$\lambda = 5920 \text{ \AA}$ (and $\lambda = 5410 \text{ \AA}$).

We then established calibration curves, giving the extinction (for each substance at the value of λ given above) as a function of concentration.

We then measured the adsorption from a solution (about 10 cm³), in which were shaken about 1.7 g of BaSO₄; all the solutions had previously been saturated with BaSO₄, and all the calibrations were carried out in solutions, containing the dye stuff, and saturated

¹ I. M. KOLTHOFF and W. M. MAC NEVIN, J. Amer. chem. Soc. 59, 1639 (1937).

² L. DE BROUCKÈRE, Ann. Chim. Belg. [10] 19, 92 (1933).

with BaSO₄; the concentration of the original solutions were (in the case of methylene blue) 11.54; 17.00; 30.8; 51.4; 115.4; 218.4 and 308.0 mg/l.

The adsorption isotherms (Fig. 2) obtained were of the Langmuir type, except that in the cases of crystal violet and methylene blue there was a decrease of adsorption at the higher concentrations; we also plotted 1/x (quantity adsorbed) as a function of 1/c (equilibrium concentration) and obtained (apart from the exception just mentioned) straight lines which could be extrapolated to 1/c = 0; this gave us x_∞; the results were:

Crystal violet: x_∞ = 0.10 mg/g BaSO₄ = 2.5 × 10⁻⁷ mole/g
Methylene blue: x_∞ = 0.066 mg/g BaSO₄ = 2.2 × 10⁻⁷ mole/g
Picric acid: x_∞ = 0.040 mg/g BaSO₄ = 1.8 × 10⁻⁷ mole/g

If we combine these Figures with our previous value for the surface area of 1 g of p.p. of BaSO₄ (= 5150 cm²), we obtain the following values for the surface area occupied by 1 mole, 1 g or 1 molecule of our dye stuffs in the adsorbed state.

	m ² /mole	m ² /g	Å ² /mole- cule
Crystal violet	206 × 10 ⁴	5 150	343
Methylene blue	234 × 10 ⁴	7 800	390
Picric acid	286 × 10 ⁴	12 400	477

On the other hand, 100 Å² seems to be a reasonable value for the surface area of a dyestuff molecule, if we consider the structure formula of the molecule and the lengths of bonds; hence the degree of occupation of the surface is found to be 30–22%.

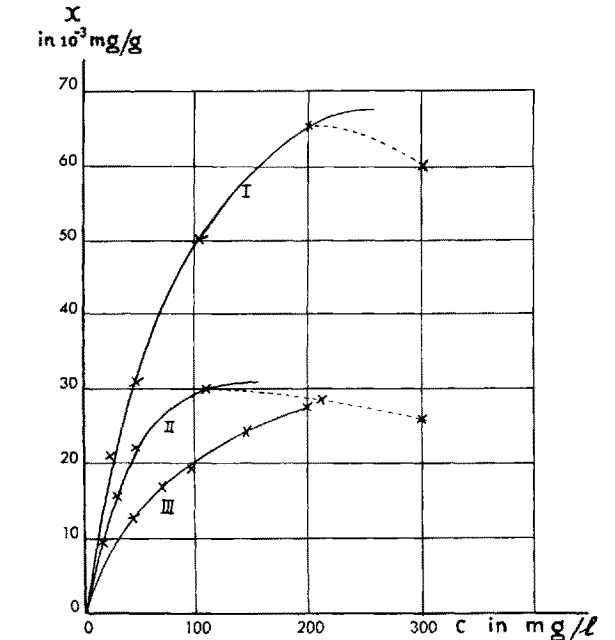


Fig. 2. – Adsorption isotherms on BaSO₄ of I.–Crystal violet; II.–Methylene blue; III.–Picric acid.

LANGMUIR¹ has treated the problem of surface occupation theoretically; his theory has empirical features (drawing from a pack of shuffled cards); the structure of the adsorbing surface is of great importance in his theory.

We decided to use the following empirical method for the determination of the maximum occupation of surface, where the influence of the structure of the adsorbing surface is neglected: we stamped a big piece of paper with a stamp in an arbitrary way, but we rejected every print covering partly an already existing print; our stamping ended with carefully stamping all places where there was still space for a print; we then counted the number of prints, and calculated the degree of occupation. This method gave a degree of occupation of 50% for a circular of moderately elliptic stamp, and 30% for a rectangular stamp (5 × 1.5 cm²).

We think, therefore, that the degree of occupation ranging from 30–22% for our molecules of rather complicated shape is not unreasonable.

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Zusammenfassung

Die spezifische Oberfläche von BaSO₄-Niederschlägen wurde bestimmt durch Messung des Austausches von Oberflächen-Ba-Ionen mit γ-radioaktiven Ba¹³¹-Ionen (spezifische Aktivität etwa 1 mc/g) einer gesättigten BaSO₄-Lösung. Die spezifische Oberfläche war 5150 cm²/g.

Dann wurden die Adsorptionsisothermen von Farbstoffen (Kristallviolett, Methylenblau und Pikrinsäure) an der Oberfläche von BaSO₄-Teilchen bestimmt. Unter der Annahme, dass jedes Farbstoffmolekül im adsorbierten Zustand eine Oberfläche von 100 Å² einnimmt, ergab sich ein maximaler Besetzungsgrad von 22–30%.

Segregation of Bivalents in Meiosis Induced by Chemicals

Analysis of the effects of chemicals on grasshopper chromosomes made in this laboratory has shown that among the major changes induced by a variety of chemicals on meiosis is the remarkable phenomenon of the bodily movement of bivalents to the poles in anaphase 1, instead of their separation into univalents. An account of it was presented as seen in urethane affected meiosis¹; but a more recent examination of material treated with a number of other chemicals has demonstrated this as a widespread phenomenon. In such clearly different chemicals as the nitrogen mustards and sodium ribose nucleate, meiosis is affected in such a manner as to present the appearance of a clear segregation of bivalents.

Poecilocera picta (Acrididae) was used as the animal for study. Specimens were injected with the following chemicals in normal saline: (a) ethyl urethane, 2%, (b) nitrogen mustard [di(2-chloroethyl)-methyl-amine-hydrochloride], 0.1%, and (c) sodium ribose nucleate (from yeast), 0.1%. In each case, 0.4 ml of the solution was injected into the posterior abdomen of the grasshopper. At various intervals after injection, the testes were removed and fixed in Carnoy's fluid and Feulgen squashes were made. Sections were also cut (10 μ thick) and stained in Feulgen-light green and Heidenhain's haematoxylin. With urethane, 6 h after injection, about half the number of meiotic anaphases showed bivalent

¹ I. LANGMUIR, J. chem. Soc. 1940, 335. ¹ P. K. NAMBIAR, Cytologia (in press).